ATOMIC & MOLECULAR PHYSICS

for

CSIR-UGC-NET/JRF|GATE

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Chapter 1

Bohr-Sommerfeld Theory of Hydrogen Atom

Bohr Atomic Model:

In 1913, Niel Bohr developed a model of atomic structure. This model is based on following postulates.

(1) An atomic electron revolve in the circular orbits around the nucleus under the influence of coulombic attraction between the nucleus and electron.

(2) Electron can revolve only in those circular orbits for which magnitude of angular momentum is integral multiple of $\frac{h}{2\pi}$ or $\hbar$. These orbits are known as stationary orbits.

i.e., $|\vec{L}| = m_e v_n r_n = \frac{nh}{2\pi}$, where $n = 1, 2, 3, ...$

(3) When an electron makes a transition from one orbit of total energy (E_i) to another orbit of total energy (E_f), then emission or absorption takes place in the form of electromagnetic radiation. The energy of emitted or absorbed photon $h\nu = E_i \sim E_f$. For emission $(E_i > E_f)$, the frequency of radiation is given by

$$\nu = \left(\frac{E_i - E_f}{h}\right).$$

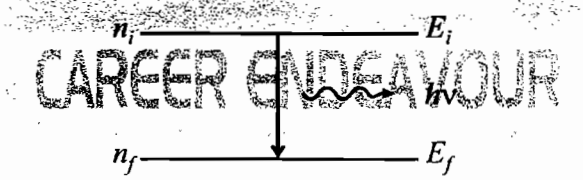

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Figure : 1.1 Electronic transition from E_i to E_f (emission)

Bohr's atomic model is applicable to only one electron atoms. These atoms are ${}_1H^1$, ${}_1H^2$, ${}_1H^3$, He^+, Li^{2+},... positronium and muonic atoms etc.

Explanation of spectra of Hydrogen like atom :

Let the charge on nucleus be +Ze and charge of electron be $-e$ and mass m_e. As according to Bohr's theory, electrons revolve in circular orbit around the nucleus, the required centripetal force is provided by the Coulombic attraction between nucleus and the electron.

Thus, $\frac{mv_n^2}{r_n} = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(e)}{r_n^2}$

$\Rightarrow \frac{m^2 v_n^2 r_n^2}{r_n} = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n^2}\cdot mr_n^2$ (multiplying by mr_n^2 on both sides)

$$\Rightarrow \left(\frac{nh}{2\pi}\right)^2 \cdot \frac{1}{r_n} = \frac{Ze^2 m}{4\pi\varepsilon_0}$$

$$\Rightarrow r_n = \frac{n^2 h^2 \varepsilon_0}{\pi m Ze^2}; n = 1, 2, 3, \ldots$$

$$\Rightarrow r_n \propto n^2$$

For Hydrogen atom,

$$Z = 1,\ n = 1,\ r_1 = \frac{h^2\varepsilon_0}{\pi m e^2} = \frac{(6.6\times10^{-34})^2 \times (8.85\times10^{-12})}{(3.14)\times(9.1\times10^{-31})\times(1.6\times10^{-19})^2} = 5.27\times10^{-11}\ \text{m}$$

$$\Rightarrow \qquad r_1 = 0.53\ \text{Å}$$

This is called as Bohr's radius (a_0) and for n =2, $r_2 = 4r_1 = 4\times0.53\text{Å} = 2.12$ Å. Also $mv_n r_n = \frac{nh}{2\pi}$

$$\Rightarrow \qquad v_n = \frac{nh}{2\pi m r_n} = \frac{nh}{2\pi m\left(\frac{n^2h^2\varepsilon_0}{\pi m Ze^2}\right)}$$

$$\Rightarrow \qquad v_n = \frac{Ze^2}{2nh\varepsilon_0},\ \text{where } n = 1, 2, \ldots$$

Total energy of the Hydrogen like atom,

$$E_n = K.E. + P.E. = \frac{1}{2}m\left[\frac{Ze^2}{2nh\varepsilon_0}\right]^2 + \left[-\frac{Ze^2}{4\pi\varepsilon_0\left(\frac{n^2h^2\varepsilon_0}{\pi m Ze^2}\right)}\right]$$

$$= \frac{mZ^2e^4}{8n^2h^2\varepsilon_0^2} - \frac{mZ^2e^4}{4n^2h^2\varepsilon_0^2} = -\frac{1}{8}\left(\frac{mZ^2e^4}{n^2h^2\varepsilon_0^2}\right) = -\frac{me^4Z^2}{8\varepsilon_0^2h^2}\left[\frac{1}{n^2}\right] = -\frac{me^4}{8\varepsilon_0^2h^3c}\left[\frac{Z^2hc}{n^2}\right]$$

(multiplying by *hc* in numerator and denominator)

$$\Rightarrow E_n = -R_\infty Z^2 hc\left(\frac{1}{n^2}\right) \text{ where, } R_\infty = \frac{me^4}{8\varepsilon_0^2h^3c};\ \text{this constant is known as Rydberg constant .}$$

For Hydrogen atom, $E_n = -\frac{R_\infty hc}{n^2}$

The value of $R_\infty = \frac{me^4}{8\varepsilon_0^2ch^3} = \frac{(9.1\times10^{-31})\times(1.6\times10^{-19})^4}{8\times(8.85\times10^{-12})^2\times(3\times10^8)\times(6.6\times10^{-34})^3}$

$$\Rightarrow \qquad R_\infty = 1.0974\times10^7/\text{m}$$

Now, energy $(E_n) = -\frac{1.0974\times10^7\times6.6\times10^{-34}\times3\times10^8}{n^2}$ Joule.

$$E_n = -\frac{13.6}{n^2}\text{ eV}$$

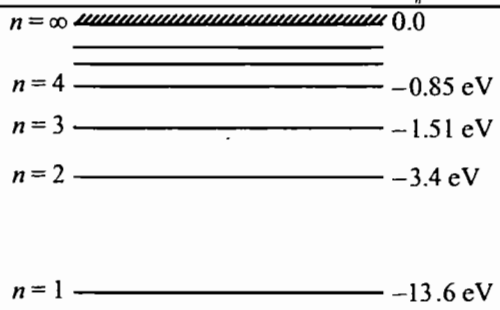
For $n = 1$, $E_1 = -13.6$ eV

For $n = 2$, $E_2 = -3.4$ eV

For $n = 3$, $E_3 = -1.51$ eV

⋮ ⋮

For $n = \infty$, $E_\infty = 0$ eV



Minimum energy required to remove the electron completely from the orbit is called binding energy or ionization energy.

Binding energy for Hydrogen atom is $E_B = +13.6$ eV.

Ionization energy for Hydrogen atom = + 13.6 eV

Ionization energy for Lithium atom = 5.39 eV

Sometimes energy is expressed in terms of term value (T).

$$T = \frac{E}{hc} = \bar{\nu}$$

where, $\bar{\nu}$ is called as wave number. The unit of $\bar{\nu}$ is m^{-1} or cm^{-1}.

Thus, wave number of n^{th} state, $\bar{\nu}_n = -\frac{13.6}{n^2 hc} Z^2 m^{-1}$ (in M.K.S. units)

Since, E is measured in joule, h is measured in joule/sec and c is measured in m/sec. Thus, unit of $\bar{\nu}_n$ is m^{-1}.

Finite nuclear mass correction in the expression of energy :

To convert, two body problem into one body, we always use concept of reduced mass (μ).

$$\mu = \left[\frac{m_{nucleus} \times m_{electron}}{m_{nucleus} + m_{electron}}\right]$$

If $m_{nucleus} \to \infty$ then $\mu = m_e$.

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Ratio of mass of proton to mass of electron = 1836. i.e., $\frac{m_p}{m_e} = 1836$.

For Hydrogen, $\mu_H = \frac{(1836 \times m_e) \times m_e}{(1836 m_e + m_e)} = \frac{1836 m_e^2}{1837 m_e} = \frac{1836 m_e}{1837}$

$\mu_H < m_e \Rightarrow R_H < R_\infty$

Thus, the binding energy, $E_B = +13.6$ eV will decrease by a factor $\left(\frac{1836}{1837}\right)$ and the energy of n^{th} orbit,

$$E_n = -\frac{13.6}{n^2}\left(\frac{1836}{1837}\right) \text{eV}$$

Positronium atom : Positronium atom is the bound state of an electron and a positron. The positron is anti-particle of electron. In positronium, nucleus will contain one positron with charge + e.

Thus, reduced mass of positronium atom, $\mu_{positronium} = \frac{m_e \cdot m_e}{m_e + m_e} = \frac{m_e}{2}$ and energy of n^{th} state of positronium atom,

$$(E_n)_{\text{positronium}} = -\frac{13.6}{2n^2}\text{ eV} \Rightarrow (E_n)_{\text{positronium}} = -\frac{6.8}{n^2}\text{ eV}$$

The speed of electron will be same as in Hydrogen i.e., $v_{\text{positronium}} = v_H$ (for any state).

The radius of the orbit will be twice of the orbit of hydrogen atom.

i.e., $r_{\text{positronium}} = 2r_{\text{hydrogen}}$ (for any state)

The wave number, $\bar{\nu} \propto E \propto R$ and Rydberg constant, $R_{\text{positronium}} = \frac{R_H}{2}$.

Muonic atom : The mass of muon $(m_\mu) = 207\, m_e$. The muonic atom is hydrogen like atom in which electron is replaced by muon. The reduced mass of muonic atom,

$$\mu_{\text{muonic}} = \frac{m_p \cdot m_\mu}{m_p + m_\mu} = \frac{(1836\, m_e) \times (207\, m_e)}{(1836\, m_e + 207\, m_e)}$$

$$\mu_\mu = \left(\frac{1836 \times 207}{1836 + 207}\right) m_e \Rightarrow \mu_\mu = 186\, m_e$$

The binding energy $= 13.6 \times 186$ eV $= 2529.6$ eV.

Time period and frequency of revolution in hydrogen like atom :

The number of revolution in unit second is called as frequency of revolutions.

The time period of revolution,

$$T_n = \frac{2\pi r_n}{v_n}$$

The velocity in hydrogen like atom, $v_n = \frac{Ze^2}{2\varepsilon_0 nh}$ and radius, $r_n = \frac{n^2h^2\varepsilon_0}{\pi m Ze^2}$

$$\therefore\ T_n = 2\pi\left(\frac{n^2h^2\varepsilon_0}{\pi m Ze^2}\right) \times \left(\frac{2\varepsilon_0 nh}{Ze^2}\right) \Rightarrow T_n = \frac{4\varepsilon_0^2 n^3 h^3}{mZ^2e^4}$$

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which is required expression of time period of electron in n^{th} state.

Therefore, frequency of revolution in n^{th} orbit,

$$f_n = \frac{1}{T_n} = \frac{mZ^2e^4}{4\varepsilon_0^2 n^3 h^3}$$

which is required expression of frequency of revolution.

Various series observed in hydrogen atom spectrum :

(1) Lyman series : In this series, all the transitions start from $n_i = 2, 3, 4, \ldots\ldots$ and terminate at $n_f = 1$.

$$\because\ \text{wave number } \bar{\nu} = \frac{1}{\lambda} = R_\infty\left[\frac{1}{n_{f^2}} - \frac{1}{n_{i^2}}\right] \Rightarrow \frac{1}{\lambda} = R_\infty\left[\frac{1}{1^2} - \frac{1}{n_{i^2}}\right]$$

where, $n_i = 2, 3, 4, 5, \ldots, \infty$.

Minimum wavelength for this series :

The λ_{min} will give $\bar{\nu}\left(\frac{1}{\lambda_{min}}\right)$ maximum and this occurs when $n_i = \infty$.

$\therefore \quad \lambda_{min} = \frac{1}{R_\infty} \approx 911\,\text{Å}$

Maximum wavelength for this series :

For λ = maximum, $\frac{1}{\lambda}$ = minimum

This occurs when $n_i = 2$

$\therefore \quad \lambda_{max} = \frac{4}{3R_\infty} \cong 1215\,\text{Å}$

i.e., $\lambda_{max} = \frac{4}{3}\lambda_{min}$ (for Lyman series)

Note: (i) For Lyman series, all the spectral lines lie in the ultraviolet region of electromagnetic spectrum.

(ii) First lines of Lyman series $(n_i = 2 \text{ to } n_f = 1)$ is called as L_α line, second line $(n_i = 3 \text{ to } n_f = 1)$ is called as L_β line, similarly for L_γ, L_δ,.... so on.

(2) Balmer series : In this series, all the transitions starts from $n_i = 3, 4, 5, \ldots$ and terminates at $n_f = 2$.

Therefore, wave number $\bar{\nu} = \frac{1}{\lambda} = R_\infty\left[\frac{1}{n_{f^2}} - \frac{1}{n_{i^2}}\right] = R_\infty\left[\frac{1}{2^2} - \frac{1}{n_i^2}\right]$, where, $n_i = 3, 4, 5, \ldots, \infty$.

Note: (i) All the spectral lines of the Balmer series lies in the visible region of the electromagnetic spectrum.

(ii) The first line $(n_i = 3 \text{ to } n_f = 2)$ of Balmer series is called as H_α, second line $(n_i = 4 \text{ to } n_f = 2)$ is H_β and third line is H_γ,... so on.

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Minimum wavelength of this series :

The minimum wavelength λ_{min} will give $\left(\frac{1}{\lambda_{min}}\right)$ maximum

$\therefore \quad \bar{\nu}_{max} = \frac{1}{\lambda_{min}} = R_\infty\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] \Rightarrow \lambda_{min} = \frac{4}{R_\infty} \cong 3644\,\text{Å}$

Maximum wavelength of this series :

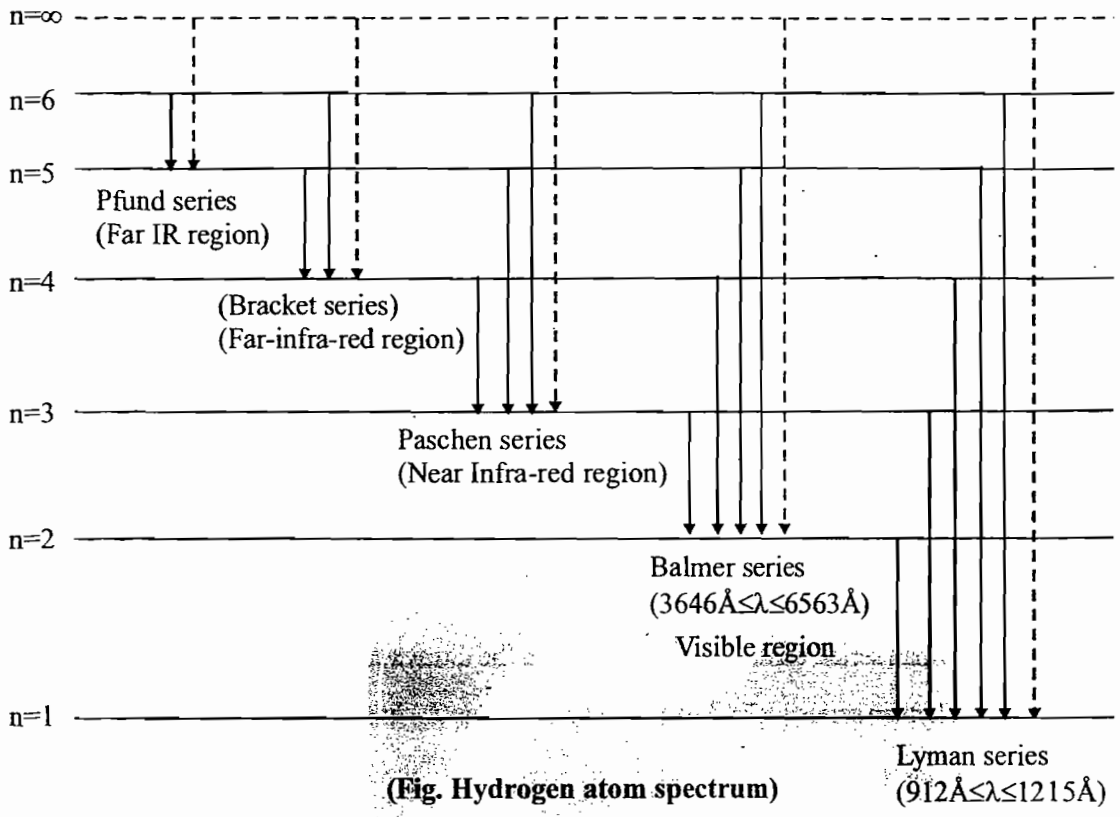
The maximum wavelength λ_{max} will give $\left(\frac{1}{\lambda_{max}}\right)$ minimum.

$\therefore \quad \bar{\nu}_{min} = \frac{1}{\lambda_{max}} = R_\infty\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \Rightarrow \lambda_{max} = \frac{36\,R_\infty}{5} \Rightarrow \lambda_{max} = 6559\,\text{Å}$

(3) Paschen series : In this series, all the transitions start from $n_f = 4, 5, 6, \ldots\ldots$ and terminates at $n_i = 3$.

$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = R_\infty\left[\frac{1}{n_{f^2}} - \frac{1}{n_{i^2}}\right] = R_\infty\left[\frac{1}{(3)^2} - \frac{1}{n_{i^2}}\right] = R_\infty\left[\frac{1}{9} - \frac{1}{n_{i^2}}\right]$, where $n_i = 4, 5, 6, \ldots, \infty$.

Note: Paschen series lies in infrared region.



(Fig. Hydrogen atom spectrum)

(4) Brackett series : In this series, all the transitions start from $n_f = 5, 6, 7, \ldots\ldots$ and terminates at $n_i = 4$.

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = R_\infty \left[\frac{1}{n_{f^2}} - \frac{1}{n_{i^2}} \right] = R_\infty \left[\frac{1}{(4)^2} - \frac{1}{n_{i^2}} \right] = R_\infty \left[\frac{1}{16} - \frac{1}{n_{i^2}} \right], \text{ where } n_i = 5, 6, 7, \ldots, \infty.$$

Note: Brackett series lies in far infrared region.

(5) Pfund series : In this series, all the transitions start from $n_f = 6, 7, 8, \ldots\ldots$ and terminates at $n_i = 5$.

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = R_\infty \left[\frac{1}{n_{f^2}} - \frac{1}{n_{i^2}} \right] = R_\infty \left[\frac{1}{(5)^2} - \frac{1}{n_{i^2}} \right] \Rightarrow \bar{\nu} = R_\infty \left[\frac{1}{25} - \frac{1}{n_{i^2}} \right], \text{ where } n_i = 6, 7, 8, 9, \ldots, \infty.$$

Note: Pfund series also lies in far infrared region.

S. No.	Series	Wave number	Region	First line (Å)	Series limit (Å)
1.	Lyman	$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{1^2}-\frac{1}{n_i^2}\right); n_i=2,3,4,...$	ultraviolet	1215	911
2.	Balmer	$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{2^2}-\frac{1}{n_i^2}\right); n_i=3,4,5,...$	visible	6559	3644
3.	Paschen	$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{3^2}-\frac{1}{n_i^2}\right); n_i=4,5,6,...$	infrared	18746	8201
4.	Brackett	$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{4^2}-\frac{1}{n_i^2}\right); n_i=5,6,7,...$	infrared	40501	14580
5.	Pfund	$\bar{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{5^2}-\frac{1}{n_i^2}\right); n_i=6,7,8,...$	far infrared	74558	22782

De-Broglie's interpretation of Bohr's atomic model :

According to de-Broglie's hypothesis, electron can move only in those orbits for which

$$2\pi r_n = n\lambda \qquad \text{... (i)}$$

above equation is called as de-Broglie's condition of stationary orbit.

According to de-Broglie, orbiting electron behaves as a wave and wavelength of the wave associated with electron is given by

$$\lambda=\frac{h}{p}=\frac{h}{mv_n} \qquad \text{... (ii)}$$

From equation (i), putting the value of λ in equation (ii), we get

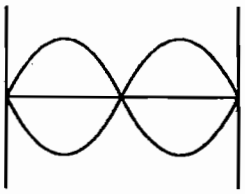
$$\frac{2\pi r_n}{n}=\frac{h}{mv_n} \Rightarrow mv_n r_n=\frac{nh}{2\pi}$$

$$\Rightarrow \quad |\vec{L}|=\frac{nh}{2\pi} \qquad \left[\because mv_n r_n=|\vec{L}|=\text{angular momentum}\right]$$

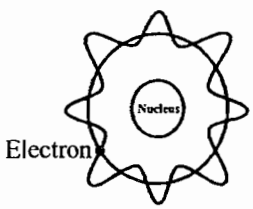
which is Bohr's condition of stationary orbit.

De-Broglie have also proved that the electron do not radiate energy in stationary orbit.

According to de-Broglie, moving electron behave as a wave and while moving in stationary orbit, the condition $2\pi r_n = n\lambda$ also satisfied.



(Standing wave)



While moving in stationary orbit, electron have particle as well as wave nature. The wave associated with electron will form a standing wave i.e. energy will be localized. The wave will not propagate in the medium ($v_g = 0$) and there will be no loss of energy. Hence, these electrons will not radiate energy.

Bohr's correspondence principle:

Neither in Bohr's theory nor in Planck's quantum which Bohr utilised, any attempt was made in developing any new theory of atomic mechanics. Hence they were *ad hoc* in nature. Bohr however noted from the energy expression that as the quantum number n becomes very large, the successive values of the allowed energy differ very little from each other and appear almost continuous. Also, as the spectral lines tend to the series limit they crowd so much that the spectrum appears continuous. In this context, Bohr in 1923 enunciated an important principle called the correspondence principle. It states that the behaviour of an atomic system as predicted by quantum theory tends asymptotically (i.e. corresponds) to that expected in classical theory in transitions involving states of large quantum numbers. Bohr's correspondence principle forms an important guideline in formulating the laws of atomic mechanics.

We give here an elementry deduction (illustration ?) of the principle.

The frequency of revolution f of the electron in an orbit of radius r is

$$f = \frac{\text{electron speed}}{\text{orbit circumference}} = \frac{\text{v}}{2\pi r}$$

Substituting the values of v and r

$$\text{v}_n = \frac{Ze^2}{2 \in_0 nh} \quad ; \quad r = \frac{n^2 h^2 \in_0}{\pi m Z e^2}$$

$$f = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3}\left(\frac{2}{n^3}\right) \qquad ...(i)$$

A radiated frequency in quantum theory however is, from (vii) of Art 3.5,

$$v = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_1^2}\right)$$

$$= \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3}\frac{(n_i - n_f)(n_i + n_f)}{n_i^2 n_f^2}$$

$$= \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3}\frac{(2np - p^2)}{n^2(n-p)^2} \qquad ...(ii)$$

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writing n for n_i and $n - p$ $(p = 1, 2, 3, ...)$ for n_f.

For very large n_i and n_f, $n \gg p$ and we obtain

$$\frac{2np - p^2}{n^2(n-p)^2} \simeq \frac{2np}{n^4}$$

Therefore, from (ii) above, $v = \frac{mZ^2 e^4}{8\varepsilon_0^2 h^3}\left(\frac{2p}{n^3}\right)$

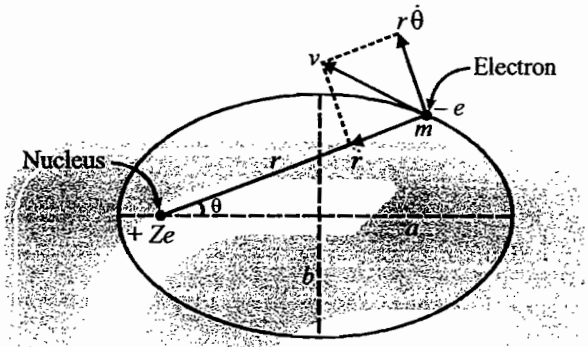
When $p = 1$, $v = f$, the frequency of rotation of electron, from (i). Harmonies of this frequency are radiated when $p = 2, 3, 4, ...$ Thus for very large quantum numbers, the classical orbit frequency equals the quantum theory frequency.

Sommerfeld's Extension of Bohr's Model

In Bohr's model of hydrogen atom, the electron could move only in circular orbits. This restriction was entirely arbitrary. Moreover, inspite of the striking numerical agreements, the Bohr's model could not explain the "fine structure" of the hydrogen spectral lines. The fine structure is splitting of the spectral lines into several close, distinct components when observed under equipment of high resolution. This means that each Bohr's energy level in hydrogen atom actually consists of several components which are close together in energy.

Sommerfeld, in 1916, in an attempt to explain the fine structure, expected Bohr's model by assuming that the electron could move in elliptic orbits also, in addition to Bohr's circular orbits. He evaluated the size and shape of the allowed elliptic orbits, as well as the total energy of an electron moving in such an orbit.

Let us consider the motion of an electron (mass m, charge $-e$) in an elliptic orbit, with nucleus (charge $+Ze$) at one focus (figure). The instantaneous position of the electron can be described in terms of the plane polar coordinates r and θ, which, being periodic functions of time, must be quantised separately.



If p_r and p_θ be the radial and the angular momenta of the electron, then according to Wilson-Sommerfeld quantisation rules, we have

$$\oint p_r\, dr = n_r h \qquad \text{... (i)}$$

and $$\int_0^{2\pi} p_\theta\, d\theta = k\, h, \qquad \text{... (ii)}$$

where n_r and k are integers, called 'radial' and 'azimuthal' quantum numbers respectively.

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The second integral is easily evaluated because according to classical mechanics, the angular momentum p_θ of any isolated system is constant. Thus,

$$p_\theta \int_0^{2\pi} d\theta = k\, h \text{ or } p_\theta = \frac{k\, h}{2\pi}. \qquad \text{... (iii)}$$

This restriction on the orbital angular momentum is the same as in Bohr circular orbit theory.
To evaluate the first integral, let us write

$$p_r = m\dot{r} \qquad \text{... (iv)}$$

and $$p_\theta = mr^2\dot{\theta} \qquad \text{... (v)}$$

where r and $\dot{\theta}$ are the radial and the angular components of the velocity of the electron.
Now, the polar equation of the ellipse is

$$\frac{1}{r} = \frac{1}{a}\frac{1-\varepsilon\cos\theta}{1-\varepsilon^2}. \qquad \text{...(vi)}$$

where $\sqrt{1-\varepsilon^2} = \frac{b}{a}$ (ratio of semi-minor to semi-major axis).

Taking logarithmic differentiation of r with respect to θ, we get

$$-\frac{1}{r^2}\frac{dr}{d\theta}=\frac{1}{a}\frac{\varepsilon\sin\theta}{1-\varepsilon^2}$$

or $$\frac{1}{r}\frac{dr}{d\theta}=-\frac{\varepsilon\sin\theta}{1-\varepsilon\cos\theta}$$ [from eq. (vi)]

or $$\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2=\frac{\varepsilon^2\sin^2\theta}{(1-\varepsilon\cos\theta)^2}.$$ ... (vii)

Now, $p_r = m\dot{r} = m\frac{dr}{dt} = m\frac{dr}{d\theta}\frac{d\theta}{dt} = m\frac{dr}{d\theta}\dot{\theta}$. Using eq. (v), we have

$$p_r=\frac{p_\theta}{r^2}\frac{dr}{d\theta}$$ ... (viii)

Also, $$dr=\frac{dr}{d\theta}d\theta.$$

$\therefore$ $$p_r\,dr=p_\theta\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 d\theta.$$

Using equation (vii), we have $p_r\,dr=p_\theta\frac{\varepsilon^2\sin^2\theta\,d\theta}{(1-\varepsilon\cos\theta)^2}$.

Hence the integral in equation (i) becomes $p_\theta\int_0^{2\pi}\frac{\varepsilon^2\sin^2\theta\,d\theta}{(1-\varepsilon\cos\theta)^2}=n_r h.$

The value of this definite integral is $2\pi\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right)$. Therefore, $2\pi\,p_\theta\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right)=n_r h.$

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But $p_\theta=\frac{kh}{2\pi}$, by equation (iii),

$\therefore$ $$kh\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right)=n_r h \quad \textbf{or} \quad \frac{1}{\sqrt{1-\varepsilon^2}}-1=\frac{n_r}{k}$$

or $$\frac{1}{\sqrt{1-\varepsilon^2}}=\frac{n_r}{k}+1=\frac{n_r+k}{k} \quad \textbf{or} \quad \sqrt{1-\varepsilon^2}=\frac{k}{n_r+k}.$$

But $\sqrt{1-\varepsilon^2}=\frac{b}{a}$, a property of ellipse.

$\therefore$ $$\frac{b}{a}=\frac{k}{n_r+k}.$$ ... (ix)

Since, n_r and k are integers, we may put $n_r + k = n$, where n is called 'principal' or 'total' quantum number. In order to exclude "pendulum" orbits passing through the nucleus, Sommerfeld postulated that the azimuthal quantum number $k \neq 0^*$, that is, $k = 1, 2, 3, ...$

The radial quantum number n_r, however, takes the zero value for which the orbit is circular. That is

$n_r = 0, 1, 2, 3, ...$

Therefore, n can take on the values : $n_r = 1, 2, 3, 4, ...$

For a given value of n, the k can assume only the values $k = 1, 2, 3, ..., n$.

The equation (ix) now becomes $\frac{b}{a} = \frac{k}{n}$. ... (x)

This is the quantum condition for the elliptic orbits. Out of all the classical possible ellipses, ***the electron can move only in those orbits for which the ratio of the minor to the major axis is the ratio of two integers.***

This quantities the size and the shape of the allowed elliptic orbits.

Total Energy of Electron in allowed Orbit : Let us now calculate the total energy E of an electron in a quantised elliptic orbit. The energy is the sum of the kinetic energy K and the potential energy U. That is

$$E = K + U = \frac{1}{2} m(\dot{r}^2 + r^2\dot{\theta}^2) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}.$$

Using equation (iv) and (v), we have

$$E = \frac{1}{2m}\left\{p_r^2 + \frac{p_\theta^2}{r^2}\right\} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}.$$

Again, using equation (viii), we have

$$E = \frac{p_\theta^2}{2mr^2}\left[\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 + 1\right] - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

or $$\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 = \frac{2mEr^2}{p_\theta^2} - 1 + \frac{mZe^2 r}{2\pi\varepsilon_0 p_\theta^2}. \quad \text{... (xi)}$$

Now, from equation (vi), we have

$$1 - \varepsilon\cos\theta = \frac{a(1-\varepsilon^2)}{r} \text{ or } \varepsilon^2\cos^2\theta = \left\{1 - \frac{a(1-\varepsilon^2)}{r}\right\}^2$$

or $$\varepsilon^2\sin^2\theta = \varepsilon^2 - \varepsilon^2\cos^2\theta = \varepsilon^2 - \left\{1 - \frac{a(1-\varepsilon^2)}{r}\right\}^2 = \varepsilon^2 - 1 - \frac{a^2(1-\varepsilon^2)^2}{r^2} + \frac{2a(1-\varepsilon^2)}{r}$$

or $$\frac{\varepsilon^2\sin^2\theta}{(1-\varepsilon\cos\theta)^2} = \frac{r^2}{a^2(1-\varepsilon^2)}\left\{-(1-\varepsilon^2) - \frac{a^2(1-\varepsilon^2)^2}{r^2} + \frac{2a(1-\varepsilon^2)}{r}\right\}$$

$$= -\frac{r^2}{a^2(1-\varepsilon^2)} - 1 + \frac{2r}{a(1-\varepsilon^2)}.$$

Substituting this in equation (vii), we have $\left(\frac{1}{r}\frac{dr}{d\theta}\right)^2 = -\frac{r^2}{a^2(1-\varepsilon^2)} - 1 + \frac{2r}{a(1-\varepsilon^2)}$.

This is identical with equation (xi). Hence, we can compare the coefficients of r^2 and r in these two equations.

Then, we have $\frac{2mE}{p_\theta^2} = -\frac{1}{a^2(1-\varepsilon^2)}$ and $\frac{mZe^2}{2\pi\varepsilon_0 p_\theta^2} = \frac{2}{a(1-\varepsilon^2)}$.

But $1-\varepsilon^2 = \frac{b^2}{a^2}$. Therefore, the last two equations become

$$\frac{2mE}{p_\theta^2} = -\frac{1}{b^2} \qquad \text{... (xii)}$$

and $$\frac{mZe^2}{2\pi\varepsilon_0 p_\theta^2} = \frac{2a}{b^2} \qquad \text{... (xiii)}$$

Dividing equation (xii) by the square of equation (xiii), we have

$$\frac{8\pi^2\varepsilon_0^2 E p_\theta^2}{mZ^2e^4} = -\frac{b^2}{4a^2} \text{ or } E = -\frac{mZ^2e^4(b^2/a^2)}{32\pi^2\varepsilon_0^2 p_\theta^2}.$$

But $p_\theta = \frac{kh}{2\pi}$ by equation (iii), and $\frac{b}{a} = \frac{k}{n}$ by equation (x).

$$\therefore \qquad E = -\frac{mZ^2e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right).$$

This energy expression is exactly the same as for the Bohr's circular orbit. That is, the energy of the electron still depends only on the principal quantum number n, and is independent of the azimuthal quantum number k.

Size and Shape of Sommerfeld's Elliptic Orbits : From equation (xiii), we have $a = \frac{mZe^2b^2}{4\pi\varepsilon_0 p_\theta^2}$.

Applying $p_\theta = \frac{kh}{2\pi}$, and $\frac{b}{a} = \frac{k}{n}$ so that $b = \frac{ak}{n}$, we have

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$$a = \frac{\pi mZe^2a^2}{n^2h^2\varepsilon_0} \text{ or } a = \frac{n^2h^2\varepsilon_0}{\pi mZe^2}. \qquad \text{... (xv)}$$

Now, $\frac{h^2\varepsilon_0}{\pi me^2} = a_0$ (say), the radius of the smallest Bohr orbit of hydrogen atom. Hence, we may write

$$a = \frac{n^2}{Z}a_0 \qquad \text{... (xvi)}$$

Further, using $b = \frac{ak}{n}$, we have

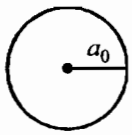
$$b = \frac{nk}{Z}a_0 \qquad \text{... (xvii)}$$

Equation (xvi) and (xvii) determine the size and shape of Sommerfeld's elliptic orbits.

Now, the theory predicts that for a given value of $n(=k+n_r)$, k can take n possible different values $(k=1, 2, 3,..., n)$. This means that for a given n, there are n orbits of different eccentricities (according to the condition $\frac{b}{a}=\frac{k}{n}$) which can be occupied by the electron. Let us consider the first few cases of hydrogen atom $(Z=1)$.

For $n=1$; we have $k=1$, so that from equations (xvi) and (xvii), we have $a=a_0$ and $b=a_0$.

This is a circular orbit of radius a_0 (figure) which is exactly the same as the Bohr's orbit.



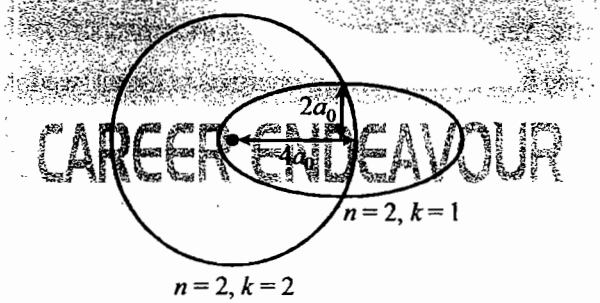
$n=1, k=1$

For $n=2$, we have

(i) $k=2$ so that $\left.\begin{matrix} a=4a_0 \\ b=4a_0 \end{matrix}\right\}$

(ii) $k=1$ so that $\left.\begin{matrix} a=4a_0 \\ b=2a_0 \end{matrix}\right\}$

Thus, for $n=2$, we have a Bohr's circular orbit of radius $4a_0$, and an elliptic orbit with semi-major axis $4a_0$ and semi-minor axis $2a_0$ (figure).



$n=2, k=1$

$n=2, k=2$

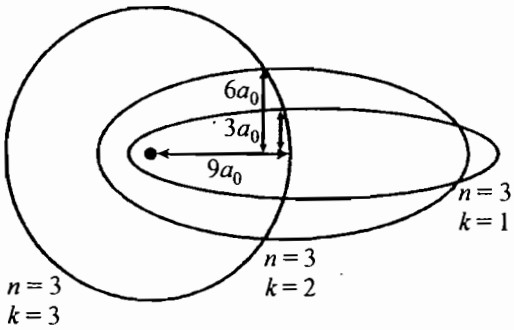
For $n=3$, there are types of possible orbits :

(i) $k=3$ so that $\left.\begin{matrix} a=9a_0 \\ b=9a_0 \end{matrix}\right\}$

(ii) $k=2$ so that $\left.\begin{matrix} a=9a_0 \\ b=6a_0 \end{matrix}\right\}$

(iii) $k=1$ so that $\left.\begin{matrix} a=9a_0 \\ b=3a_0 \end{matrix}\right\}$

Thus, out of the three possible orbits, one is the Bohr's circular orbit of radiu $9a_0$, the second is an elliptic orbit of semi-major axis $9a_0$ and semi-minor axis $6a_0$, and the third is an elliptic orbit with semi-major axis $9a_0$ and semi-minor axis $3a_0$ (figure).



We see that corresponding to each value of the principal quantum number n, there are n different allowed orbits. One of these is circular, just the orbit described by the original Bohr theory. The others are elliptic, all having the same semi-major axis as the radius of the circular orbit, but different semi-minor axes. The orbit having the lowest k is most elliptic.

But, describe the very different paths followed by the electron moving in different possible orbits for a given n, the total energy of the electron is the same. This means that **Sommerfeld's introduction of elliptic orbits adds no new energy levels,** and hence fails to explain the fine structure. The several orbits characterised by a common value of energy are said to be 'degenerate'.

To designate an orbit of given n and k values, the value of n is followed by one of the letters $s, p, d, f, g,...$ according as $k = 1, 2, 3, 4, 5,...$ respectively. For example, the state $n = 3, k = 1$ is written as $3s$; and that $n = 3, k = 2$ and $3p$. It is seen that the s-electron orbit (lowest k) is most elliptical in any family of orbits having same major axis (same n).

Shortcomings of Bohr-Sommerfeld Theory

The Bohr-Sommerfeld theory was quite successful in explaining many experimental observations on the structure of atoms and simple spectra. Yet, it was not free from shortcomings.

(i) Although the theory told how to calculate the energies of the allowed states of an atom, and the frequency of radiation emitted or absorbed in transitions between allowed states; but it could not tell how to calculate the rate at which such transitions take place. As such, it could not explain the variation in intensity of the spectral lines.

(ii) The theory is applicable only to one-electron atoms like hydrogen, hydrogen isotopes, singly-ionised helium, etc. It fails when applied to the neutral helium atom which has only two electrons.

(iii) As we have seen, even in hydrogen-like atoms the theory become silent on the observed fine-structure of spectral lines.

(iv) No logical reason was given for the introduction of quantum numbers. The quantum numbers were introduced by Bohr as a postulate and adhoc selection rules were adopted to explain the observed lines.

(v) The theory did not throw any light on the distribution and arrangement of electrons in atoms.

(vi) The success of the theory in dealing with the effect of a magnetic field on spectral lines was only partial. It could not explain automalous Zeeman effect.

SOLVED PROBLEMS

1. The wavelength of the first line of the Lyman series of Hydrogen is 1215Å. Calculate the wavelength of the second line of the series and the series limit.

Soln. The wavelengths of the lines of the Lyman series of Hydrogen atom are given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right); n = 2, 3, 4, \ldots$$

For the first line $(\lambda = 1215\,\text{Å})$, $n = 2$.

$$\therefore \frac{1}{1215\,\text{Å}} = \frac{3}{4}R_H$$

or $$R_H = \frac{4}{3\times(1215\,\text{Å})}.$$

For the second line $n = 3$.

$$\therefore \frac{1}{\lambda} = \frac{4}{3\times(1215\,\text{Å})}\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = \frac{4}{3\times(1215\,\text{Å})}\times\frac{8}{9}$$

or $$\lambda = \frac{3\times(1215\,\text{Å})\times 9}{4\times 8} = 1025\,\text{Å}$$

For the series limit, $n = \infty$.

$$\therefore \lambda_\infty = \frac{1}{R_H} = \frac{3\times(1215\,\text{Å})}{4} = 911\,\text{Å}.$$

2. Calculate the ionisation potential for He^+, Li^{++} and Positronium atom.

Soln. The ionisation potential of an atom corresponds to the energy of the atom in the ground state. For one-electron atom, the ground-state energy is (ignoring effect of finite nuclear mass)

$$E_1 = -R_\infty Z^2 hc$$

or $$E_1 \propto Z^2$$

(i) For He^+ and H, we have Z = 2 and 1 respectively.

$$\therefore \frac{E_{He^+}}{E_H} = 4.$$

Hence the ionisation potential of He^+ is 4 times that of H.
Hence, ionisation potential of $He^+ = 4 \times 13.6 = +54.4$ eV.
(ii) For Li^{++} and H, we have Z = 3 and 1 respectively.

$$\therefore \frac{E_{Li^{++}}}{E_H} = 9.$$

Hence the ionisation potential of Li^{++} is 9 times that of H.
Hence, ionisation potential of $Li^{++} = 9 \times 13.6 = +122.4$ eV.
(iii) The positron has the same mass m as the electron and has equal but positive charge. The reduced mass of the electron-positron atom is therefore

$$\mu = \frac{(m)(m)}{m+m} = \frac{1}{2}m$$

while the reduced mass of electron in Hydrogen is very nearly m.

The Rydberg constant $\left(\frac{\mu e^4}{8\varepsilon_0^2 h^3 c}\right)$ for positronium, R_P, is therefore half that for Hydrogen (with infinitely heavy nucleus). Thus

$$R_P = \frac{1}{2}R_\infty .$$

The energy states of the positronium atom would then be given by

$$(E_P)_n = -\frac{R_P Z^2 hc}{n^2} = -\frac{R_\infty Z^2 hc}{2n^2} . \qquad ...(i)$$

The corresponding expression for Hydrogen atom (with infinitely heavy nucleus) is

$$(E_H)_n = -\frac{R_\infty Z^2 hc}{n^2} . \qquad ...(ii)$$

Now, Z = 1 for positronium atom as well as for Hydrogen atom. Hence, we conclude from equation (i) and (ii) that the ionisation energy, which is numerically equal to the energy of the lowest state (n = 1), of positronium atom is half of that of Hydrogen atom.

Hence, ionisation potential of positronium atom = +6.8 eV.

3. How many revolutions does an electron in the n = 2 state of H-atom make before dropping to the n = 1 state? The average life time of an excited state is 10^{-8} sec.

Soln. Let v be the velocity of electron (mass m, charge e) revolving in a Bohr orbit of Hydrogen atom (Z = 1) of radius r. The condition of mechanical stability of the electron is

$$\frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} .$$

The quantum condition is

$$mvr = \frac{nh}{2\pi}, \qquad n = 1, 2, 3, \ldots$$

These two equation give $v = \frac{e^2}{2nh\varepsilon_0}$ and $r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2}$.

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The number of revolutions of the electron in the orbit per second is

$$f = \frac{v}{2\pi r} = \frac{me^4}{4\varepsilon_0^2 n^3 h^3} = \frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{2c}{n^3}\right) = R_\infty\left(\frac{2c}{n^3}\right).$$

For the n = 2 state, the frequency of revolution is

$$f = \frac{R_\infty c}{4}$$

Substituting the given value of R_∞, and the known value of c, we get

$$f = \frac{\left(1.097\times10^7 m^{-1}\right)\left(3.0\times10^8 ms^{-1}\right)}{4}$$

$$= 8.2\times10^{14} s^{-1}$$

Hence the number of revolutions of the electron in its life-time of 10^{-8} second is

$$= \left(8.2\times10^{14} s^{-1}\right)\times10^{-8} s = 8.2\times10^6 .$$

4. If the wavelength of the first line of the Balmer series in the hydrogen is λ, then the wavelength of the first line of the Lyman series is **[GATE-2002]**

(a) $\left(\frac{27}{5}\right)\lambda$ (b) $\left(\frac{5}{27}\right)\lambda$ (c) $\left(\frac{32}{27}\right)\lambda$ (d) $\left(\frac{27}{32}\right)\lambda$

Soln. For Balmer series, the first line is given by

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

$$\Rightarrow \quad \frac{1}{\lambda} = R\left[\frac{1}{4} - \frac{1}{9}\right] = \frac{5R}{36}$$

$$\Rightarrow \quad R = \frac{36}{5\lambda} \qquad \ldots (i)$$

Now, the first line of the Lyman series is given by

$$\frac{1}{\lambda_{\text{Lyman}}} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = R\left[1 - \frac{1}{4}\right] = \frac{3R}{4} = \frac{3}{4}\left[\frac{36}{5\lambda}\right] = \frac{27}{5\lambda}$$

$$\Rightarrow \quad \frac{1}{\lambda_{\text{Lyman}}} = \frac{5\lambda}{27}.$$

Hence, correct option is (b).

5. If R_1 is the value of the Rydberg constant assuming mass of the nucleus to be infinitely large compared to that of an electron, and if R_2 is the Rydberg constant taking nuclear mass to be 7500 times the mass of the electron, then the ratio R_2/R_1 is **[GATE-2002]**

(a) a little less than unity (b) a little more than unity
(c) infinitely small (d) infinitely large

Soln. Rydberg constant for an atom with infinitely large nucleus is given by

$$R_\infty = \frac{me^4}{8\varepsilon_0^2 ch^3} \qquad \ldots (i)$$

and Rydberg constant for an atom with nucleus of finite mass M is given by

$$R_M = \frac{\mu e^4}{8\varepsilon_0^2 ch^3} \qquad \ldots (ii)$$

where, μ is reduced mass and is given by $\mu = \frac{mM}{(m+M)}$.

$$\therefore \quad R_M = \left(\frac{mM}{m+M}\right)\cdot\frac{e^4}{(8\varepsilon_0^2 ch^3)} = \left(\frac{M}{m+M}\right)\cdot\left(\frac{me^4}{8\varepsilon_0^2 ch^3}\right)$$

$$\Rightarrow \quad R_M = \frac{1}{\left(1+\frac{m}{M}\right)} R_\infty \qquad \ldots (iii)$$

According to given question $R_\infty = R_1$ and $R_M = R_2$ and $\frac{m}{M} = \frac{1}{(7500)}$

Thus, equation (iii),

$$\Rightarrow \quad R_2 = \frac{1}{\left(1+\frac{1}{7500}\right)} R_1 \Rightarrow \frac{R_2}{R_1} = \frac{7500}{7501} \text{ i.e., } \frac{R_2}{R_1} < 1$$

Hence, correct option is (a).

6. Consider the Bohr model of the hydrogen atom. If α is the fine structure constant, then the velocity of the electron in its lowest orbit is **[JEST 2012]**

(a) $\frac{c}{1+\alpha}$ (b) $\frac{c}{1+\alpha^2}$ or $(1-\alpha)c$ (c) $\alpha^2 c$ (d) αc

Soln. The velocity of the electron in Hydrogen atom's lowest orbit is

$$v = \frac{Ze^2}{2nh\epsilon_0} = \frac{e^2}{2h\epsilon_0} \quad (\because \text{for hydrogen } Z = 1 \text{ and for first orbit } n = 1) \qquad \ldots (i)$$

The fine structure constant α is given by

$$\alpha = \frac{e^2}{2\epsilon_0 hc} \qquad \ldots (ii)$$

Thus, dividing equation (ii) by (i), we get

$$\frac{v}{\alpha} = \frac{e^2}{2h\epsilon_0} \times \frac{2\epsilon_0 hc}{e^2} \Rightarrow \frac{v}{\alpha} = c \Rightarrow \boxed{v = c\alpha}$$

Hence, correct option is (d).

7. The binding energy of the hydrogen atom (electron bound to proton) is -13.6 eV. The binding energy of positronium (electron bound to positron) is **[JEST 2012]**

(a) 13.6/2 eV (b) 13.6/1810 eV (c) 13.6× 1810 eV (d) 13.6 × 2 eV

Soln. Binding energy (E_B) $\propto$ reduced mass (μ).

For electron bound to proton, $\mu = \frac{mM}{m+M} = \frac{(m_e)(1836\,m_e)}{m_e + 1836\,m_e} = \frac{1836}{1837} m_e \approx m_e$

For electron bound to position, $\mu = \frac{mM}{m+M} = \frac{m_e . m_e}{m_e + m_e} = \frac{m_e}{2}$

$$\therefore \quad \frac{\text{Binding energy of hydrogen atom}}{\text{Binding energy of positronium atom}} = \frac{m_e}{\left(m_e/2\right)} \Rightarrow \frac{[E_B]_{Hydrogen}}{[E_B]_{Positronium}} = 2$$

$$\Rightarrow \quad [E_B]_{Positronium} = \frac{1}{2} \times [E_B]_{Hydrogen} = \frac{1}{2} \times 13.6\,\text{eV}$$

Hence, correct option is (a).

8. If a proton were ten times lighter, then the ground state energy of the electron in a hydrogen atom would be **[JEST 2013]**

(a) less (b) more (c) same

(d) less, more or equal depending on the electron mass

Soln. The energy of the electron n^{th} state (orbit) in a hydrogen atom is given by

$$E_n = \frac{-\mu Z^2 e^4}{8\epsilon_0^{\,2} h^2}\left(\frac{1}{n^2}\right) \qquad \ldots (1)$$

Where, $\mu = \dfrac{m_e M}{m_e + M}$ (where M is the mass of hydrogen nucleus)

$$\mu = \frac{m_e \cdot m_p}{m_e + m_p} \qquad \ldots (2)$$

For $m_p' = \dfrac{m_p}{10} = \dfrac{1836}{10} m_e = 183.6\, m_e$

$$\therefore \quad \mu = \frac{(m_e) \times (183.6\, m_e)}{(m_e + 183.6\, m_e)} = \frac{183.6}{184.6} m_e = 0.9946\, m_e \quad \Rightarrow \quad \frac{\mu}{m_e} = 0.9946$$

For normal proton of mass m_p, the ground state energy $= -13.6$ eV

For $m_p' = \dfrac{m_p}{10}$, the ground state energy $= -13.6 \times 0.9946 = -13.526$ eV

Hence, the ground state energy will be more.

Hence, correct option is (b).

9. If a proton were ten times heavier, then the ground state energy of the electron in a hydrogen atom would have been **[JEST 2014]**

(a) less (b) more (c) same (d) depends on the electron mass

Soln. For $m'_p = 10\, m_p = 10 \times 1836 m_e$

$$\therefore \quad \mu = \frac{(m_e)(18360\, m_e)}{(m_e + 18360\, m_e)} = \frac{18360}{18361} m_e = 0.999945536\, m_e \text{ i.e. } \frac{\mu}{m_e} = 0.99995$$

For normal proton of mass m_p, the ground state energy $= -13.6$ eV

Now for $m'_p = 10\, m_p$, the ground state energy $= -13.6 \times 0.99995$ eV $= -13.5992593$ eV > -13.6 eV

Hence, the gound state energy will be more.

Hence, correct option is (b).

10. A hydrogen atom in its ground state is collided with an electron of kinetic energy 13.377 eV. The maximum factor by which the radius of the atom would increase is **[JEST 2014]**

(a) 7 (b) 8 (c) 49 (d) 64

Soln. Energy of the electron in n^{th} orbit for hydrogen,

$$E_n = \left(-\frac{13.6}{n^2}\right) \text{eV} \qquad \ldots (i)$$

Therefore, ground state energy, $E_1 = -\dfrac{13.6}{(1)^2}$ eV $= -13.6$ eV

Since electron have kinetic energy of 13.377 eV

Therefore, difference in energy $= (-13.6) - (-13.377) = (-13.6 + 13.377)$ eV $= -0.223$ eV

Let us check which state is this ?

Since, $-\dfrac{13.6}{n^2} = -0.223 \text{ eV} \Rightarrow n^2 = \left(\dfrac{13.6}{0.223}\right) = 61$

Therefore, radius, $r_n = (n^2)\, a_0 = 61 \times a_0$

Here, $n^2 = 61 \Rightarrow n = 7.8$, i.e. the value of n lies between 7 and 8. Therefore, electron will lie in $n = 7$ state.

Thus, radius will increase 49 times.

Hence, correct option is (c).

11. If the Rydberg constant of an atom of finite nuclear mass is αR_∞, where R_∞ is the Rydberg constant corresponding to an infinite nuclear mass, the ratio of the electronic to nuclear mass of the atom is:

(a) $(1-\alpha)/\alpha$ (b) $(\alpha-1)/\alpha$ (c) $(1-\alpha)$ (d) $1/\alpha$ **[JEST 2016]**

Soln. The Rydberg constant for an atom having an infinitely heavy nucleus is

$$R_\infty = \frac{me^4}{8\epsilon_0^2 h^3 c}\text{; (where, } m \text{ is the mass of electron)} \quad \text{... (i)}$$

and for an atom having a nucleus of mass M is

$$R_M = \frac{\mu e^4}{8\epsilon_0^2 h^3 c} \quad \text{... (ii)}$$

Where, $\mu = \frac{mM}{m+M} = \frac{m}{\left(1+\frac{m}{M}\right)}$; M is nuclear mass

$$\therefore \quad R_M = \frac{me^4}{8\epsilon_0^2 h^3 c}\cdot\frac{1}{\left(1+\frac{m}{M}\right)} = \frac{R_\infty}{\left(1+\frac{m}{M}\right)} \quad \text{... (iii)}$$

According to question, $R_M = \alpha R_\infty$ ... (iv)

Comparing equation, (iii) and (iv), we get

$$\alpha R_\infty = \frac{R_\infty}{\left(1+\frac{m}{M}\right)}$$

$$\Rightarrow \quad \alpha\left(1+\frac{m}{M}\right)=1 \Rightarrow \alpha+\alpha\left(\frac{m}{M}\right)=1 \Rightarrow \alpha\left(\frac{m}{M}\right)=(1-\alpha) \Rightarrow \frac{m}{M}=\left(\frac{1-\alpha}{\alpha}\right)$$

$$\therefore \quad \frac{\text{electronic mass}}{\text{nuclear mass}} = \left(\frac{1-\alpha}{\alpha}\right)$$

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Hence, correct option is (a).

12. The velocity of an electron in the ground state of a hydrogen atom is v_H. If v_p be the velocity of an electron in the ground state of positronium, then **[TIFR 2013]**

(a) $v_p = v_H$ (b) $v_p = 2v_H$ (c) $v_p = \frac{v_H}{2}$ (d) $v_p = \sqrt{2}v_H$

Soln. The velocity of electron in the ground state of hydrogen atom is given by

(For z = 1, n = 1), $\boxed{v_H = \frac{e^2}{2h\epsilon_0}}$ .... (i)

For the positronium, the velocity of electron will be given by $\boxed{v_P = \frac{e^2}{2h\epsilon_0}}$ .... (ii)

From equation (i) and (ii), we get $\boxed{v_P = v_H}$

Hence, correct option is (a)

12. Given that the ionization energies of Hydrogen $\left({}^{1}H\right)$ and Lithium $\left({}^{3}Li\right)$ are 13.6 eV and 5.39 eV respectively. The effective nuclear charge experienced by the valence electron of the ${}^{3}Li$ atom may be estimated in terms of proton charge e as **[TIFR 2011]**

(a) 3.00 e (b) 1.59 e (c) 1.26 e (d) 0.63 e

Soln. Energy $\left(E\right) = -13.6\ eV\left(\frac{Z_{eff}^{\ 2}}{n^2}\right)$

For Li, $Z = 3$, and $E = 5.39\ eV$ and valence electron lies in $n = 2$ orbit.

$$\therefore \quad 5.39 = 13.6 \times \frac{Z_{eff}^{\ 2}}{(2)^2}$$

$$\Rightarrow \quad Z_{eff}^{\ 2} = \frac{5.39}{13.6} \times 4 \Rightarrow Z_{eff}^{\ 2} = 1.59 \Rightarrow \boxed{Z_{eff} = 1.26}$$

Thus, the effective nuclear charge = 1.26 e

Hence, correct option is (c).

13. A sample of ordinary hydrogen $\left({}_{1}^{1}\mathrm{H}\right)$ gas in a discharge tube was seen to emit the usual Balmer spectrum. On careful examination, however, it was found that the H_α line in the spectrum was split into two fine lines, one an intense line at 656.28 nm, and the other a faint line at 656.04 nm. From this, one can conclude that the gas sample had a small impurity of **[TIFR 2015]**

(a) ${}_{1}^{2}\mathrm{H}$ (b) ${}_{1}^{3}\mathrm{H}$ (c) ${}_{2}^{4}\mathrm{He}$ (d) $\mathrm{H_2O}$

Soln. For hydrogen, the wavelength of H_α line is given by

$$\frac{1}{\lambda_{H_\alpha}} = R_H\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \quad \ldots (i)$$

For unknown impurity, the wavelength of H_α line is given by

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$$\frac{1}{\lambda_X} = R_X\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \quad \ldots (ii)$$

From equation (i) and (ii), we get

$$\left(\frac{1/\lambda_{H_\alpha}}{1/\lambda_X}\right) = \frac{R_H}{R_X} \Rightarrow \frac{\left(\frac{1}{656.28}\right)}{\left(\frac{1}{656.04}\right)} = \frac{R_X}{R_X}$$

$$\Rightarrow \quad \frac{R_H}{R_X} = 0.999634302 \Rightarrow R_X = 1.000365831,\ R_H = \frac{x m_p \cdot m_e}{x m_p + m_e} = (1.000365831) \times \left(\frac{m_p \cdot m_e}{m_p + m_e}\right)$$

$\Rightarrow$ $\boxed{x = 3.04679}$. Thus, the mass of electron nucleus will be three times larger than ordinary hydrogen $\left({}_{1}^{1}\mathrm{H}\right)$. Out of given options ${}_{1}^{3}\mathrm{H}$ has 3 times larger mass. **Hence, correct option is (b)**

Chapter 2

Quantum Numbers, Electron Spin, Magnetic Dipole Moments and Vector Atom Model

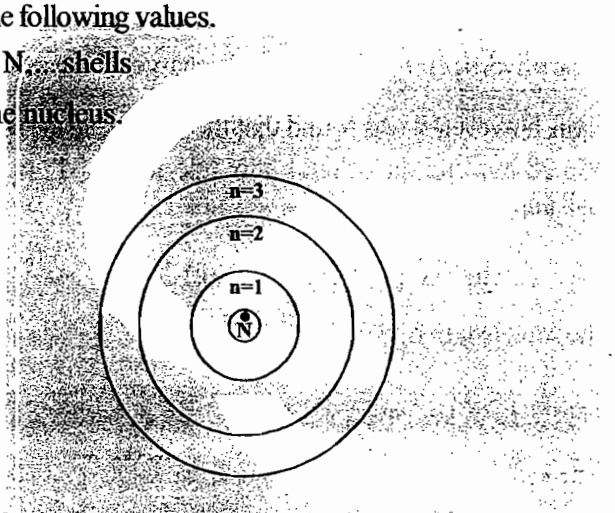
QUANTUM NUMBERS

To determine the position of an electron in an atom, we require the knowledge of following four quantum numbers. These are obtained by using quantum mechanics. These quantum numbers are as follows:

1. **Principal quantum number (n):** The principal quantum number tells us about the shell to which a particular electron belongs to. n can take the following values.

   $n = 1, 2, 3, 4$.....i.e., K, L, M, N,... shells

   $n = 1$ or K shell is nearest to the nucleus.



2. **Orbital quantum number or azimuthal quantum number (ℓ):**
   This quantum number was introduced by Sommerfeld. Azimuthal quantum numbers (ℓ) represents the subshells to which an electron belongs to. For a given shell (n), ℓ can take the following values :

   $$\ell = 0, 1, 2.....(n-1)$$

   Example:
   (a) For $n = 3$;
   $\ell = 0$, 1, 2
   (s-subshell) (p-subshell) (d-subshell)
   Number of subshells in a shell = n.
   (b) For $n = 1$, $\ell = 0$ $\Rightarrow$ s – subshell only
   and $n = 2$, $\ell = 0, 1$ $\Rightarrow$ s and p subshells.

3. **Orbital magnetic quantum number (m_ℓ):** Orbital magnetic quantum number (m_ℓ) represents the different states corresponding to a subshell (ℓ).

   m_ℓ can take the values given as

   $$m_\ell = \ell, (\ell-1).....1, 0, -1, -2....(-\ell)$$

   Example: If $\ell = 2$ (d-subshell), $m_\ell = 2, 1, 0, -1, -2$

4. Magnetic spin quantum number (m_s):

Magnetic spin quantum number (m_s) represents the orientation of an electron in an state. For an electron for spin 1/2, m_s can take the values,

$$m_s = +\frac{1}{2}, \qquad -\frac{1}{2} \qquad \begin{cases} \text{For } s = \frac{1}{2} \\ m_s = -s \text{ to } +s \text{ with difference of 1.} \end{cases}$$

$\begin{pmatrix} \text{Orientation} \\ \text{in } +z \text{ direction} \end{pmatrix}$ $\begin{pmatrix} \text{Orientation} \\ \text{in } -z \text{ direction} \end{pmatrix}$

The order of filling of an electron in different subshell is given below :

$(1s^2), (2s^2\ 2p^6), (3s^2\ 3p^6\ 3d^{10}), (4s^2\ 4p^6)$ .....

But correct configuration is $(1s)^2\ (2s^2 2p^6)\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$.....

(We see $n+\ell$ values, more $(n+\ell)$ value energy will be more; if $(n+l)$ is same for two subshell the energy of higher n subshell is more. This is why 4s is after 3p as for

$4s\ (n+\ell = 4+0)$ and $3p(n+\ell = 3+1)$

Note:

$\overset{n}{\uparrow}\overset{\ell}{\uparrow}$

(i) 3f does not exists as for $3f = n = 3$ & $\ell = 3$ and $\ell = 3$ is not possible for $n = 3$.

(ii) Maximum electrons in s, p, d, f, g, h ..... subshells are 2, 6, 10, 14, 18, 22 ..... respectively.

(iii) Total number of electrons in a shell n is $\boxed{2n^2}$.

$= 2\times$ total m_ℓ values for a given n.

$$= 2\times\sum_{\ell=0}^{n-1} 2\ell+1 = 2\times\sum_{\ell=0}^{n-1}(2\ell+1)$$

$$= 2\times\left[1+3+5....+(2n-1)\right] = 2n^2$$

(iv) Maximum electrons in an outermost shell is 8 (except n = 1 in which only 2 maximum electron can live).

(v) As atom is very small in size i.e. micro system so most of the problems related with atom are solved by quantum mechanics. In quantum mechanics, any system is represented by a wave function (ψ) which provide every information regarding the system, where ψ is known as Schrodinger wave function .

(vi) The wave funcion which represents the different states of an atom is given by

$\psi_{n,\ell,m_\ell}(r,\theta,\phi)$; r, θ, ϕ are spherical co-ordinates as the shape of the atom is spherical. But electron of an atom are revolving around nucleus in elliptical orbits/circular orbits.

(vii) For n = 2, the different states of the atom are obtained as

$$n = 2,\ \ell = 0,\ 1, \qquad \left(E_n = -\frac{13.6}{n^2}\text{eV}\right) \qquad m_\ell = 0, -1, 0, +1$$

Therefore, the total states are $\psi_{200}, \psi_{210}, \psi_{21\bar{1}}, \psi_{211}$ for H-atom, the energy of all these four states is $-\frac{13.6}{2^2} = -3.4$ eV as n = 2 for all these four states.

Thus the level $n = 2$ is four-fold degenerate or we can say that the degeneracy of $n = 2$ level is 4. (Total m_ℓ valeus).

Thus, for a level n, the degeneracy of a level is

$$= \text{Total } m_\ell \text{ values.}$$

$$= \sum_{\ell=0}^{n-1}(2\ell+1) = 1+3+5....+(2n-1)$$

$$= n^2$$

(viii) If we include spin degeneracy becomes doubled i.e. $2n^2$.

(ix) By the term degeneracy we mean, the total number of states which have the same energy.

(x) The fine structure of lineswas explained by including spin of electron.

(xi) In fine structure, the degeneracy of a level is removed.

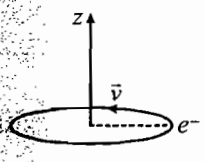
(xii) Pauli exclusion principle states "no two electrons in an atom can have all four quantum number same."

(xiii) The valence optical electrons are the outermost shell electrons in an atom.

Electron magnetic moment :

Consider an electron of mass m an charge $(-e)$ moving with velocity of magnetitude v in a circular orbit of radius r. The charge circulating in a loop constitutes a current of magnitude

$$I = \frac{e}{T} = \frac{ev}{2\pi r}$$



where, T is the orbital period of electron $= \frac{2\pi r}{v}$.

For a current I in a loop of area A, the orbital magnetic dipole moment

$$\vec{\mu}\ell = I\vec{A} = \frac{ev}{2\pi r}\pi r^2 \hat{z} = \frac{evr}{2}\hat{z}$$

Angular momentum, $\vec{L} = mvr\,\hat{z}$

$$\therefore \quad \frac{(\vec{\mu}_\ell)}{(\vec{L})} = -\frac{evr}{2 \cdot mvr} = -\frac{e}{2m}$$

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$$\therefore \quad \boxed{\vec{\mu}_\ell = \left(-\frac{e}{2m}\right)\vec{L}}$$ This reflects $\vec{\mu}_\ell$ is antiparallel to the vector $\vec{L}$.

$$\Rightarrow \quad |\vec{\mu}_\ell| = \left|-\frac{e}{2m}\right|\vec{L} = \frac{e}{2m}\sqrt{\ell(\ell+1)}\,\hbar$$

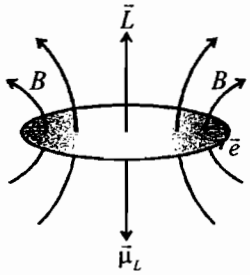
$$\Rightarrow \quad \boxed{|\vec{\mu}_\ell| = \frac{e\hbar}{2m}\sqrt{\ell(\ell+1)}}$$

Here the ratio is independent of the detail of mechanical theory used to derive it so $\vec{\mu}_\ell = -g_\ell \mu_B \vec{L}$, where

$$\mu_B = \frac{e\hbar}{2m} = \frac{eh}{4\pi m} = 9.27 \times 10^{-24}\,J/T = 5.788 \times 10^{-5}\,eV/T$$

It is called "Bohr Magneton"

The ratio of magnitude μ_ℓ of the orbital dipole moment to the magnitude L of the angular momentum for the electron is a combination of universal constant.



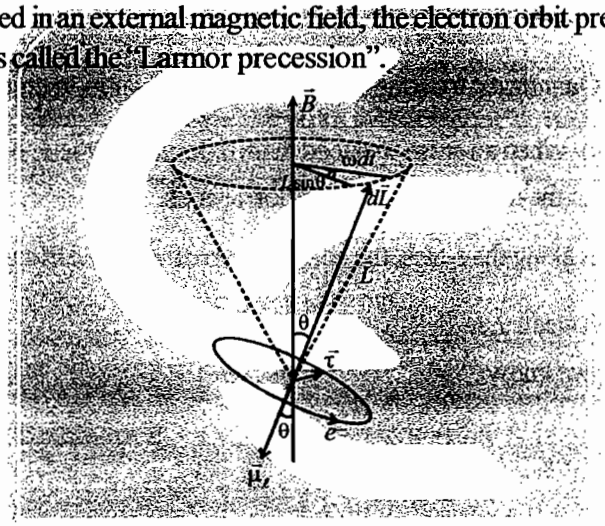
$\boxed{\frac{|\vec{\mu}_\ell|}{|\vec{L}|} = \frac{g_\ell \mu_B}{\hbar}}$; this equation is valid both for quantum and classical mechanics and g_ℓ = orbital g factor = 1

Note:

(i) The ratio of μ_ℓ to L does not depend on the size of the orbit or on the orbit frequency.

(ii) In case of elliptical orbits also, it can be shown that μ_ℓ / L is independent of the shape of the orbit.

Larmor precession : An electron moving around the nucleus of an atom is equivalent to a magnetic dipole. So when the atom is placed in an external magnetic field, the electron orbit precesses about the field direction as axis. This precession is called the "Larmor precession".



We know, $\vec{\mu}_\ell = \left(-\frac{eg_\ell}{2m}\right)\vec{L}$ here $g_\ell = 1$ when an external field $\vec{B}$ is applied, the dipole experiences a torque

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$\vec{\tau} = \vec{\mu}_\ell \times \vec{B} = \mu_\ell B \sin\theta$.

which is always perpendicular to $\vec{L}$. But $\vec{\tau} = \frac{d\vec{L}}{dt}$ so the torque causes a change in $\vec{L}$ perpendicular to it, i.e. its direction changes and it starts precessing about $\vec{B}$ with the angle of precession remaining constant.

If the precession velocity is "ω" then $\vec{L}$ precesses an angle "ωdt" in time dt.

$$\therefore \quad \omega dt = d\phi = \frac{|d\vec{L}|}{|\vec{L}|\sin\theta}$$

$$\Rightarrow \quad \omega = \frac{|d\vec{L}|}{dt} \cdot \frac{1}{|\vec{L}|\sin\theta} = \frac{|\vec{\tau}|}{|\vec{L}|\sin\theta} = \frac{|\vec{\mu}_\ell|}{|\vec{L}|\sin\theta}$$

$$\therefore \quad \omega = \frac{|\vec{\mu}_\ell|}{|\vec{L}|} B$$

or $\omega = \frac{g_\ell e}{2m} B$ Larmor angular frequency

$$\therefore \quad \text{Larmor frequency, } f = \frac{\omega}{2\pi} = \frac{g_\ell e}{4\pi m} B$$

$$\boxed{f = \frac{g_\ell eB}{4\pi m}}$$

Note: Larmor frequency is independent of the orientation angle θ between $\vec{L}$ and field direction $\vec{B}$.

The sense of the precession is in the direction of $\vec{B}$.

This theorem is of considerable importance in atomic structure as it enables an easy calculation of energy levels in the presence of an external magnetic field.

Space Quantization : Quantization of one component of angular momentum $\vec{L}$ or $\vec{S}$ in any given direction is called space quantization. When an atom is placed in an external magnetic field $\vec{B}$, the electron orbit or angular momentum precess about the magnetic field direction as axis.

If the magnetic field $\vec{B}$ is along the z-axis, the components of $\vec{L}$ parallel to the field direction is $|\vec{L}_z| = |\vec{L}| \cos\theta$, where θ is the angle between $\vec{L}$ and $\vec{B}$.

Quantum mechanically, we know

$$|\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \qquad \ell = 0, 1, 2, \ldots$$

and $L_z = m_\ell \hbar \qquad m_\ell = 0, \pm 1, \ldots, \pm \ell$

where, ℓ and m_ℓ are orbital and magnetic quantum number respectively.

$$\therefore \quad \cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

For a given ℓ, there are $(2\ell+1)$ possible values of m_ℓ. Thus, θ can assume $(2\ell+1)$ discrete values. Hence $\vec{L}$ can have $2\ell+1$ discrete orientation in space w.r.t. to given $\vec{B}$. This quantisation of orientation of electronic orbits in space is called "space quantisation".

For a given ℓ; $m_\ell = -\ell, (-\ell+1) \ldots\ldots, (\ell-1), (\ell)$

Since, $\sqrt{\ell(\ell+1)} > m_\ell$

$$\Rightarrow \quad \frac{m_\ell}{\sqrt{\ell(\ell+1)}} < 1$$

$$\Rightarrow \quad \cos\theta \neq 1 \quad \Rightarrow \quad \theta \neq 0$$

i.e. $\vec{\ell}$ can never be in direction of $\vec{\ell}_z$ or $\vec{B}$ or in z-direction.

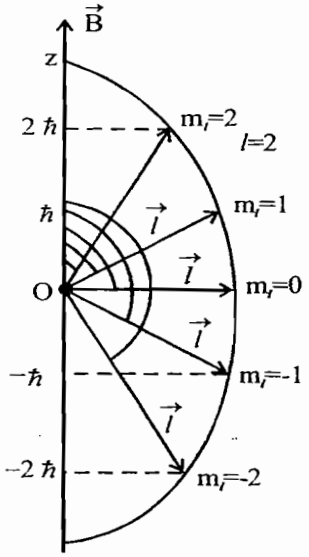
Example: For $\ell = 2$

$|\vec{L}| = \sqrt{6}\,\hbar$

$m_\ell = 0, \pm 1, \pm 2$

$L_z = 0, \pm\hbar, \pm 2\hbar$

$$\therefore \cos\theta = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} = 0, \pm\frac{1}{\sqrt{6}}, \pm\frac{2}{\sqrt{6}}$$



Note: $\vec{L}$ can never be aligned exactly parallel or antiparallel to $\vec{B}$, since m_ℓ is always smaller than $\sqrt{\ell(\ell+1)}$.

Why only one component of $\vec{L}$ quantised?

The answer is related to the fact thet $\vec{L}$ can never point in any specfic direction but instead is somewhere on a cone in space such that its projection L_z is $m_\ell\hbar$ were this not so, the uncertainty principle would be violated. If $\vec{L}$ were fixed in space, so that L_x and L_y as well as L_z had definite values, the electron would be confined to a definite plane. For instance, if L were in the z-direction, the electron would have to be in the xy-plane at all times. This can occur only if the electrons momentum component p_z in the z-direction is infinitely uncertain, which of course is impossible if it is to be part of a hydrogen atom.

Electron spin :

(a) Historical development :

- Arthur Compton in 1921 came out with an idea that an electron might posses an intrinsic angular momentum (or spin) and thus act like a magnet.
- In 1925, Pauli investigated the problem of explaining the spectra of alkali metals which were found to be not single as predicted by the Bohr model. Pauli showed that the doublet in the fine structure could be explained if the electron could exist in two distinct state.
- In the same year, in order to account for both fine structure in spectral lines and the anamalous Zeeman effect, Goudsmit and Uhlenbeck proposed that "Every electron has an intrinsic angular momentum called spin, whose magnitude is the same for all electrons. Associated with this angular momentum is a magnetic moment". They looked electron as a charged sphere spinning about its own axis.
- In 1929, the fundamental nature of electron spin was confirmed by Paul Dirac's development of relativistic quantum mechanics. He found that a particle with the mass and charge of the electron must have the intrinsic angular momentum and magnetic moment proposed for the electron by Goudsmit and Uhlenbeck.
- An excellent experiment demonstration to prove that an electron acts like a magnet was provided by the Steri-Gerlach experiment.

Theory :

(b) Goudsmit and Uhlenbeck suggested in 1925 that an electron possesses an intrinsic angular momentum called its spin, and a corresponding intrinsic magnetic moment. The spin angular momentum must be quantized both in magnitude and in spatial orientiation. If the spin angular momentum vector is denoted by $\vec{S}$, and the spin quantum number by Stern-Gerlach.

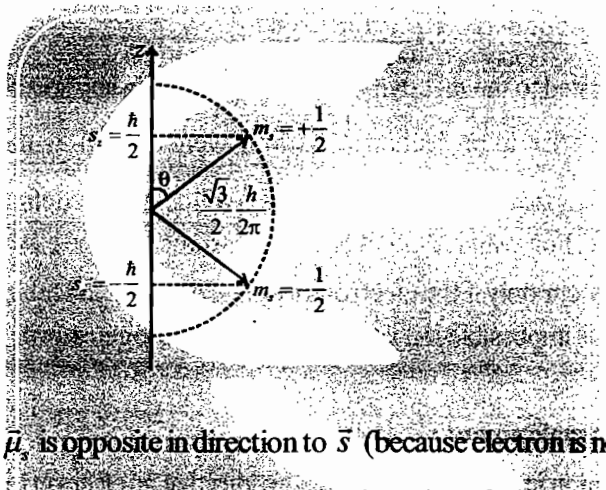
$$\boxed{\vec{S} = \sqrt{s(s+1)}\,\hbar}$$

The only value s can have is $s = \frac{1}{2}$. Therefore, $|\vec{S}| = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar = \frac{\sqrt{3}}{2}\hbar$

The component of $\vec{S}$ along a magnetic field parallel to the z-direction is $S_z = m_s \frac{h}{2\pi}$, where m_s is the "spin magnetic quantum number" and takes $2s+1 = 2$ values which are $+s$ and $-s$ that is $m_s = \pm\frac{1}{2}$.

Thus, $S_z = \pm\frac{1}{2}\frac{h}{2\pi}$

The electron's intrinsic magnetic moment $\vec{\mu}_s = -g_s\left(\frac{e}{2m}\right)\vec{s}$



The minus sign indicates that $\vec{\mu}_s$ is opposite in direction to $\vec{s}$ (because electron is negatively charged). The quantity g_s is called gyromagnetic ratio for electron spin. The value of which is twice the corresponding ratio $|\vec{\mu}_\ell|/|\vec{L}| = (e/2m)$ for electron orbital motion.

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The magnitude of the spin magnetic moment is $|\vec{\mu}_s| = 2\cdot\left(\frac{e}{2m}\right)|\vec{s}| = \frac{e}{m}\frac{\sqrt{3}}{2}\frac{h}{2\pi} = \frac{eh}{4m\pi}\sqrt{3} = \sqrt{3}\ \mu_B$

Therefore, $\boxed{|\vec{\mu}_s| = \sqrt{3}\ \mu_B}$, where μ_B is the Bohr magneton.

Note:

(i) The intrinsic magnetic moment of the electron is used for explaining the fine structure of spectral lines and the anomalous Zeeman effect.

(ii) An important characterisitic of particles with spin $\frac{1}{2}$ is that these particles obey Fermi Dirac statistics. They are, therefore, classified as fermions.

Vector model of an atom :

The total angular momentum of an atom results from the combination of the orbital and spin angular momenta of its electrons.

Consider an atom whose total angular momentum is provided by a single electron. (H, Li, Na etc. have single electron outside closed inner shells, the total angular momentum of a closed shell being zero).

The total angular momentum of the one-electron atom is the vector sum of $\vec{L}$ and $\vec{S}$, $\vec{J} = \vec{L} + \vec{S}$

Like all angular momenta, $\vec{J}$ is quantised in both magnitude and direction. The magnitude of $\vec{J}$ is given by

$$J = \sqrt{j(j+1)}\,\hbar \;;\; j = \ell \pm s = \ell \pm \frac{1}{2}$$

Where, j is called the "inner quantum number".

The corresponding J_z of $\vec{J}$ in the z-direction is given by

$$J_z = m_j \hbar \;;\; m_j = -j, -j+1, \ldots, j-1, j$$

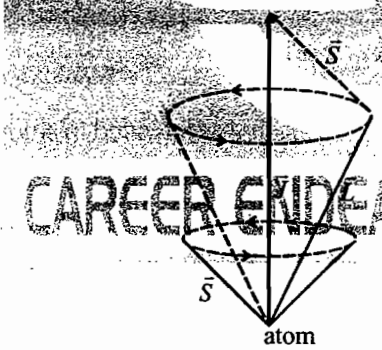
where, m_j is the magnetic quantum number.

In one-electron atom, there are only two relative orientations possible, corresponding to

$j = \ell + s$; so that $|\vec{J}| > |\vec{L}|$

$j = \ell - s$; so that $|\vec{J}| < |\vec{L}|$

The angular momenta of the atomic electron, $\vec{S}$ and $\vec{L}$ interact magnetically; which is known as "spin orbit coupling". They exert torques on each other. These internal torques do not change the magnitude of the vector $\vec{L}$ and $\vec{S}$, but cause them to process uniformly around their resultant $\vec{J}$. If the atom is in free space so that no external torques act on it, then the total angular momentum $\vec{J}$ is conserved in magnitude and direction. So, the angle between $\vec{L}$ and $\vec{S}$ would remain invariant.



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Since $\vec{J} = \vec{L} + \vec{S} \;\Rightarrow \vec{J} \cdot \vec{J} = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S})$

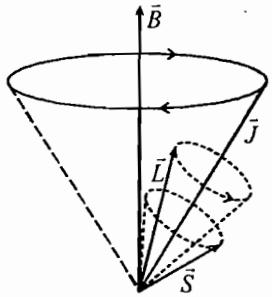
$$\Rightarrow |\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2|\vec{L}||\vec{S}|\cos(\vec{L}, \vec{S}) \text{ or } \cos(\vec{L}, \vec{S}) = \frac{|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2}{2|\vec{L}||\vec{S}|}$$

Therefore, $\cos(\vec{L}, \vec{S}) = \dfrac{j(j+1) - \ell(\ell+1) - s(s+1)}{2\sqrt{\ell(\ell+1)}\,\sqrt{s(s+1)}}$

This is the vector model of the one electron atom. It can be extended to many electron atoms.

However, in presence of external magnetic field $\vec{B}$, the total angular momentum vector $\vec{J}$ precesses about $\vec{B}$, while $\vec{L}$ and $\vec{S}$ continue to precess about $\vec{J}$. The precession of $\vec{J}$ about $\vec{B}$ is what gives rise to "Anamolous Zeeman effect" and Hyperfine structure.

The great advance made by the vector atom model lies in the fact that it offers an adequate and rational explanation of several complex atomic and spectral line explained by older models. In order to able to use effectively the vector atom model certain other important rules, such as Pauli's exclusion principle, selection intensity and interval rules and Lande's 'g' factor are required. With these additional helps, the electronic structure in atoms, the fine structure of spectral lines, the anomalous Zeeman effects, the Stark effect have been explained satisfactorily.



Vector model of the one electron atom enables us to explain the phenomena which could not be understood from Bohr-Sommerfeld theory such as fine structure, anomalous Zeeman effect and Hyperfine structure.

Stern-Gerlach Experiment:

Stern and Gerlach, in 1921, performed an experiment which demonstrated directly that an atom placed in a magnetic field can take only certain discrete orientations with respect to the field (space quantisation). It also demonstrated the existence of electron spin, thus providing an experimental verification of the vector model of atom.

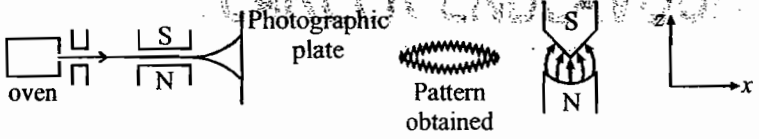
The plan of the experiment is shown in figure (below). A beam of neutral silver atoms was formed by heating silver in an oven. It was collimated by a few fine slits and then passed through a non-homogeneous magnetic field. The beam leaving the mgnetic field was received on a photographic plate P.

Physical Significance:

(i) Experimental evidence of electron spin.

(ii) Direct demonstration of space quantisation.

Experiment : The experiment of Stern and Gerlach was intended to study the deflection of atomic beams in non-uniform magnetic fields.



A beam of neutral silver atoms produced by heating silver in an oven. It was collimated by a few fine slits and then passed through a non-homogeneous magnetic field in which the field increases in z-direction. The beam leaving the magnetic field was received on a photographic plate P.

Observation : Instead of a trace of direct beam, two were obtained symmetrically situated w.r.t. the direct beam as two discrete components, one in $+z$-direction and other in $-z$-direction.

(i) The intensity of both the trace is the same.

(ii) The results obtained were independent of the choice of the z-direction.

Inference :

A magnetic dipole experiences a net deflecting force in a non-homogeneous magnetic field which depends on the orientation of the magnet in the field. Since atoms are tiny magnetic dipoles, they experience deflecting forces when passing through the field. If an atom could have any orientation in the magnetic field then for millions of atoms present in the beam all possible orientations would be obtained and the beam would be deflected into a continuous band. In the experiment however, there was no band but discrete traces on the photographic plate. This showed that the atoms passing through the magnetic field were oriented in space in

discrete directions so that beam deflected in certain discrete directions only and gave discrete traces on the plate.

Thus the experimental results are qualitatively direct proof of space quantisation of atoms.

Quantitatively : Let us consider an atom of magnetic moment μ enters a non-uniform slowly varying magnetic field B. The force acting on the atom, according to classical physics is given by $\vec{F} = \nabla(\vec{\mu} \cdot \vec{B})$.

If magnetic field $\vec{B}$ is assumed along z-direction, then average transverse force experienced by an atomic magnet transversing the (inhomogeneous) magnetic field is $F_z = \frac{\partial B_z}{\partial z}\mu_{j_z}$, where

$\frac{\partial B_z}{\partial z}$ = rate of change of field in the z-direction.

μ_{j_z} = z-component of total (orbital + spin) magnetic moment μ_j of the atom.

But, $\mu_{j_z} = g_j\left(\frac{e}{2m}\right)j_z = g_j\left(\frac{e}{2m}\right)m_j\hbar = g_j\, m_j\, \mu_B$, where $\mu_B = \frac{eh}{4\pi m}$ is the Bohr magneton, g_j is the corresponding g-factor.

Therefore, $F_z = \frac{\partial B_z}{\partial z} g_i\, m_j\, \mu_B$ or $a_z = \frac{F_z}{M} = \frac{1}{M}\frac{\partial B_z}{\partial z} g_j\, m_j\, \mu_B$ (M : mass of atom)

If v_x be the longitudinal velocity of the atoms and d the length of their path in the magnetic field then, time t for which they experience the transverse force is $t = \frac{d}{v_x}$.

But from kinetic theory, $\frac{1}{2}Mv_x^2 = \frac{3}{2}kT$

$$\Rightarrow \quad v_x = \sqrt{\frac{3kT}{M}}$$

$$\therefore \quad t = d\sqrt{\frac{M}{3kT}}$$

So, the transverse deflection suffered by atoms

$$z = \frac{1}{2}a_z t^2 = \frac{1}{2}\,\frac{1}{M}\,\frac{\partial B_z}{\partial z} g_j\, m_j\, \mu_B\, d^2\, \frac{M}{3kT}$$

$$\Rightarrow \quad \boxed{z = g_j\, m_j \frac{\frac{\partial B_z}{\partial z}\cdot \mu_B\, d^2}{6\,kT}}$$

The atomic beam would be deflected into $(2j+1)$ components corresponding to the $(2j+1)$ values of m_j, giving $(2j+1)$ traces on the plate.

For silver atoms two traces were obtained and by measuring the separation between the traces it was found that $g_j\, m_j = \pm 1$.

At the temperature of the oven, the silver atoms are in their ground state which is $2s_{1/2}$.

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$$\ell = 0,\ j = s = \frac{1}{2}$$

$$\therefore \quad \boxed{2j+1=2}$$

Hence there are two traces.

Further, $g_j = g_s = 2$, $m_j = m_s = \pm\frac{1}{2}$ as postulated by spin hypothesis.

Therefore, $g_j m_j = 2\left(\pm\frac{1}{2}\right) = \pm 1$ as experimentally observed.

Thus, it also gives evidence of electron spin.

Evidence for electronic spin :

A beam of H-atoms is used here. This atom consists of a single electron and the theory predicts, in ground state $\ell = 0$. In absence of spin of spin, therefore we would have $j = \ell = 0$ and $g_j m_j = 0$ and then beam would be unaffected by the magnetic field. However the beam split into two symmetrically deflected components corresponding to $g_j m_j = \pm 1$. This justifies the case of existence of electron spin.

Limitation of Stern-Gerlach experiment :

(i) The experiment can be carried out only for neutral atoms or molecules ; it can not be carried out for charged particles.
If the charged particles are used then the particle will move in a circular field and it will not hit the photographic plate.

(ii) If the magnetic field is uniform then it will not lead to any deflection in the particles.

(iii) The experiment can not be performed even for those neutral atoms or molecules which remain in the field for a duration shorter than $\frac{\hbar}{\mu B_z}$.

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The energy of an atom of magnetic moment $\vec{\mu}$ in a magnetic field $\vec{B}$ is $-\vec{\mu}\cdot\vec{B}$

Therefore, $E = -\mu B_z \cos\theta$

Quantum mechanically there are only two possible orientations given by $\cos\theta = \pm 1$, therefore the energy of atom in magnetic field $= \pm \mu B_z$.

So, max possible uncertainty in energy would be $\Delta E = \mu B_z$

According to uncertainty principle, $\Delta E\ \Delta t \approx \hbar$

Therefore, $\Delta t = \frac{\hbar}{\Delta E} = \frac{\hbar}{\mu B_z}$

Thus, the time during which the particle stay in non uniform magnetic field must be greater than the value of this uncertainty.

i.e., $t > \Delta t \geq \frac{\hbar}{\mu B_z}$

Angle between $\vec{\ell}$ and $\vec{s}$:

$$\vec{j} = \vec{\ell} + \vec{s}$$

$$\therefore \quad \vec{j}.\vec{j} = (\vec{\ell}+\vec{s}).(\vec{\ell}+\vec{s}) = |\vec{\ell}|^2 + |\vec{s}| + 2\vec{\ell}.\vec{s}$$

$$\Rightarrow \quad 2\vec{\ell}.\vec{s} = |\vec{j}|^2 - |\vec{\ell}|^2 - |\vec{s}|^2$$

$$\Rightarrow \quad 2|\vec{\ell}||\vec{s}|\cos\theta = |\vec{j}|^2 - |\vec{j}|^2 - |\vec{s}|$$

$$\Rightarrow \quad \boxed{\cos\theta \text{ or } \cos(\vec{\ell}.\vec{s}) = \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2\sqrt{\ell(\ell+1)}\sqrt{s(s+1)}}}$$

Angle between $\vec{j}$ and $\vec{l}$:

As $\vec{j} = \vec{\ell} + \vec{s}$

$$\Rightarrow \quad \vec{s} = \vec{j} - \vec{\ell}$$

$$\Rightarrow \quad \vec{s}.\vec{s} = (\vec{j} - \vec{\ell}).(\vec{j}.\vec{\ell})$$

$$\Rightarrow \quad |\vec{s}|^2 = |\vec{j}|^2 + |\vec{\ell}|^2 - 2\vec{j}.\vec{\ell}$$

$$\Rightarrow \quad 2\vec{j}.\vec{\ell} = |\vec{j}|^2 + |\vec{\ell}|^2 - |\vec{s}|^2$$

$$\Rightarrow \quad \boxed{\cos\theta = \cos(\vec{j}.\vec{\ell}) = \frac{j(j+\ell) + \ell(\ell+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{\ell(\ell+1)}}}$$

Angle between $\vec{j}$ and $\vec{s}$:

$$\Rightarrow \quad \vec{\ell} = \vec{j} - \vec{s} \qquad \Rightarrow \qquad \vec{\ell}.\vec{\ell} = (\vec{j} - \vec{s}).(\vec{j} - \vec{s})$$

$$\Rightarrow \quad |\vec{\ell}|^2 = |\vec{j}|^2 + |\vec{s}|^2 - 2\vec{j}.\vec{s} \qquad \Rightarrow \qquad 2\vec{j}.\vec{s} = |\vec{j}|^2 + |\vec{s}|^2 - |\vec{\ell}|^2$$

$$\Rightarrow \quad 2|\vec{j}||\vec{s}|\cos\theta = |\vec{j}|^2 + |\vec{s}|^2 - |\vec{\ell}|^2$$

$$\Rightarrow \quad \boxed{\cos\theta = \cos(\vec{j}.\vec{s}) = \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2\sqrt{j(j+1)}\sqrt{s(s+1)}}}$$

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For electron total angular momentum, orbital angular momentum and spin angular momentum are denoted by $\vec{j}$, $\vec{\ell}$ and $\vec{s}$ respectively. While for atom or for a system of two or more electron, these are denoted by $\vec{J}$, $\vec{L}$ and $\vec{S}$ respectively. For one electron (system) atom :

$\vec{j} = \vec{J}$, $\vec{\ell} = \vec{L}$ and $\vec{s} = \vec{S}$.

SOLVED PROBLEMS

1. Which one of the following is a fermion? **[GATE-2014]**

(a) α particle (b) ${}_4Be^7$ nucleus (c) Hydrogen atom (d) Deuteron

Soln. Fermions have half integral spin. Proton, electron, neutron are fermions and have 1/2-spin.
(a) spins of two neutrons and two protons will pair up in α-particle and resultant will be zero.
(b) In ${}_4Be^7$ nucleus, the resultant spin will be half integer.
(c) In case of hydrogen atom, spin of one proton and one electron will give resultant spin an integer.
(d) In case of deutron, two nucleus will give total spin an integer.
Hence fermion will be ${}_4Be^7$.

2. There are four electrons in the 3*d* shell of an isolated atom. The total magnetic moment of the atom in units of Bohr magneton is _____. **[GATE 2016]**

Soln. Since, in 3d shell, there are four electrons. All the magnetic moments will cancel out each other. Thus, the total magnetic moment of these electrons will be zero.
Hence correct answer is (0).

3. A thin uniform ring carrying charge Q and mass M rotates about its axis. What is the gyromagnetic ratio (defined as ratio of magnetic dipole moment to the angular momentum) of this ring? **[JEST 2013]**

(a) $Q/(2\pi M)$ (b) Q/M (c) $Q/(2M)$ (d) $Q/(\pi M)$

Soln. The megnetic dipole moment is given by

$$\mu = i \times A \qquad ...(1)$$

If the ring has charge Q, than current $i = \frac{Q}{T} = \frac{Q}{2\pi R} \times v$

$$= \frac{Qv}{2\pi R} \qquad ...(2)$$

and area off ring $A = \pi R^2$ ... (3)

Putting values of i & A from equation (2) and (3) in equation (1), we get

$$\mu = \frac{Qv}{2\pi R} \cdot \pi R^2$$

$$\mu = \frac{QvR}{2}$$

$$\Rightarrow \quad \mu = \frac{Q\ MvR}{2m}$$

$$\Rightarrow \quad \frac{Q}{2m} L \qquad \{\text{Where L = mVR is the angular momentum}\}$$

$$\Rightarrow \quad \frac{\mu}{L} = \frac{Q}{2m}$$

is the ratio of magnetic dipole moment to the angular momentum i.e. gyromagnetic ratio $= \frac{Q}{2m}$

Hence, correct option is (c).

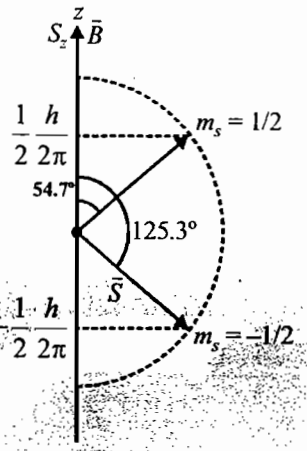
4. Calculate the two possible orientations of spin vector $\vec{S}$ with respect to a magnetic field $\vec{B}$.

Soln. Let the magnetic field $\vec{B}$ be along the *z*-axis. The magnitude of the spin angular momentum $\vec{S}$ and its *z*-component are quantised according to the relations

$$S = \sqrt{s(s+1)}\,\frac{h}{2\pi}, \qquad s = \frac{1}{2}$$

and $$S_z = m_s \frac{h}{2\pi}, \qquad m_s = \pm\frac{1}{2}$$

Hence, as clear from that figure, the angle θ between $\vec{S}$ and the z-axis is determined by the quantum numbers m_s and s, according as $\cos\theta = \frac{S_z}{S} = \frac{m_s}{\sqrt{s(s+1)}} = \frac{2}{\sqrt{3}}\,m_s$. $\left[\because\ s = \frac{1}{2}\right]$



For $m_s = +\frac{1}{2}$, we have $\cos\theta = +\frac{1}{\sqrt{3}} = 0.577$. Therefore, $\theta = \cos^{-1}(0.577) = 54.7°$.

For $m_s = -\frac{1}{2}$, we have $\cos\theta = -\frac{1}{\sqrt{3}} = -0.577$. Therefore, $\theta = \cos^{-1}(-0.577) = 125.3°$.

5. Obtain the magnitude of spin magnetic dipole moment of an electron in terms of Bohr magneton.

Soln. The spin magnetic moment $\vec{\mu}_s$ of electron is related to its spin angular momentum $\vec{S}$ by $\vec{\mu}_s = -g_s\left(\frac{e}{2m}\right)\vec{S}$.

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The magnitude of spin magnetic moment is $\mu_s = g_s\frac{e}{2m}S$.

Now, $g_s = 2$ and $S = \sqrt{s(s+1)}\,\frac{h}{2\pi} = \frac{\sqrt{3}}{2}\frac{h}{2\pi}$, as $s = \frac{1}{2}$. Therefore, $\mu_s = 2\left(\frac{e}{2m}\right)\frac{\sqrt{3}}{2}\frac{h}{2\pi} = \sqrt{3}\,\frac{eh}{4\pi m}$.

But, $\frac{eh}{4\pi m} = \mu_B$, the Bohr magneton. Therefore, $\mu_s = \sqrt{3}\,\mu_B$.

6. A beam of electrons enters a uniform magnetic field of flux density 1.2 tesla. Calculate the energy difference between electrons whose spins are parallel and antiparallel to the field.

Soln. An electron has an intrinsic (spin) angular momentum $\vec{S}$ and an intrinsic magnetic dipole moment $\vec{\mu}_s$, which are related by $\vec{\mu}_s = -g_s\left(\frac{e}{2m}\right)\vec{S}$, where $g_s = 2$, $S = \sqrt{s(s+1)}\,\frac{h}{2\pi}$ and $s = \frac{1}{2}$.

Let the magnetic field $\vec{B}$ be along the z-axis. The magnitude of the z-component of the magnetic moment is $\mu_{sz} = g_s\left(\frac{e}{2m}\right)S_z$, where S_z is the z-component of the spin angular momentum and is given by $S_z = m_s\frac{h}{2\pi}$,

where the quantum number $m_s = \pm\frac{1}{2}$, depending upon whether S_z is parallel or antiparallel to the z-axis.

Thus, $\mu_{sz} = g_s\left(\frac{e}{2m}\right)m_s\frac{h}{2\pi} = 2\left(\frac{e}{2m}\right)\left(\pm\frac{1}{2}\right)\frac{h}{2\pi} = \pm\frac{eh}{4\pi m}$.

Now, the magnetic orientational potential energy of a dipole of moment $\vec{\mu_s}$ in a magnetic field $\vec{B}$ is given by $U_m = -\vec{\mu_s}\cdot\vec{B} = -\mu_{sz}B$, where μ_{sz} is the scalar magnitude of $\vec{\mu_s}$ in the direction of the magnetic field.

Thus, $U_m = \pm\frac{eh}{4\pi m}B$. The difference in energy of electrons having spin parallel and antiparallel to the field is

$$\Delta U_m = \frac{ehB}{4\pi m} - \left(-\frac{ehB}{4\pi m}\right) = \frac{ehB}{2\pi m}.$$

Substituting the known values, of e, h and m ; and the given value of B, we get

$$\Delta U_m = \frac{(1{\cdot}60\times10^{-19}\text{ C})\times(6{\cdot}63\times10^{-34}\text{ Js})\times(1{\cdot}2\text{ N/A-m})}{2\times3{\cdot}14\times(9{\cdot}1\times10^{-31}\text{ kg})} = 2{\cdot}23\times10^{-23}\text{ J}.$$

But $1\text{ eV} = 1{\cdot}60\times10^{-19}$ J.

Therefore, $\Delta U_m = \frac{2{\cdot}23\times10^{-23}\text{ J}}{1{\cdot}60\times10^{-19}\text{ J/eV}} = 1{\cdot}39\times10^{-4}\text{ eV}$.

7. An electron in a particular state of hydrogen atom has a magnetic potential energy of about 10^{-23} J. Estimate the magnitude of the magnetic field acting on the spin magnetic moment of the electron which is of the order of 1 Bohr magneton.

Soln. $U_m = -\vec{\mu_s}\cdot\vec{B}$.

So, $|U_m| = \mu_s B$.

Given : $|U_m| = 10^{-23}$ J and $\mu_s \sim \mu_B = 9{\cdot}27\times10^{-24}\text{ A m}^2 \approx 10^{-23}\text{ A m}^2$

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Therefore, $B \sim \frac{10^{-23}\text{ J}}{10^{-23}\text{ A m}^2} \sim \frac{10^{-23}\text{ N m}}{10^{-23}\text{ A m}^2} \sim 1\frac{\text{N}}{\text{A m}} \sim 1$ tesla.

8. For an electron orbit with quantum number $l = 2$, state the possible values of the components of angular momentum along a specified direction.

Soln. The component of total angular momentum along a specified direction (z-axis) is quantised, and takes values given by $J_z = m_j\frac{h}{2\pi}$, where m_j is the magnetic quantum number corresponding to the inner quantum number j.

For the given electron, we have $l = 2$ (electron) and of course $s = \frac{1}{2}$.

The two possible values of j are $j = l \pm s = 2 \pm \frac{1}{2} = \frac{5}{2}$ and $\frac{3}{2}$.

For $j=\frac{5}{2}$, the possible values of m_j are $m_j=\frac{5}{2},\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2},-\frac{5}{2}$.

For $j=\frac{3}{2}$, the possible values of m_j are $m_j=\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2}$.

The values differ by integers. Thus, the possible values of the z-components of total angular momentum are

$$\pm\frac{5}{2}\left(\frac{h}{2\pi}\right),\pm\frac{3}{2}\left(\frac{h}{2\pi}\right),\pm\frac{1}{2}\left(\frac{h}{2\pi}\right).$$

9. Calculate the possible orientations of the total angular momentum vector $\vec{J}$ corresponding to $j=\frac{3}{2}$ with respect to a magnetic field along the z-axis.

Soln. The magnitude of the total angular momentum and its z-component are quantised according to the relations

$$J=\sqrt{j(j+1)}\frac{h}{2\pi} \text{ and } J_z=m_j\frac{h}{2\pi}.$$

For $j=\frac{3}{2}$, we have $m_j=\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2}$.

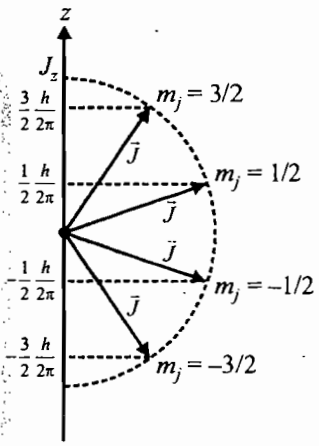
The angle θ between $\vec{J}$ and the z-axis is determined by m_j and j, according as $\cos\theta=\frac{J_z}{J}=\frac{m_j}{\sqrt{j(j+1)}}$.

Now, $\sqrt{j(j+1)}=\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)}=\frac{\sqrt{15}}{2}$. Therefore, $\cos\theta=\frac{2m_j}{\sqrt{15}}$

For $m_j=\frac{3}{2},\frac{1}{2},-\frac{1}{2},-\frac{3}{2}$, we have $\cos\theta=0.775, 0.258, -0.258, -0.775$.

Therefore, $\theta=39.2°, 75.0°, 105°, 140.8°$

The orientations of $\vec{J}$ with respect to z-axis are shown in the figure.



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10. Determine the possible terms of a one-electron atom corresponding to $n=3$ and compute the angle between $\vec{L}$ and $\vec{S}$ vectors for the term $^2D_{5/2}$.

Soln. For the principal quantum number $n=3$, the orbital quantum number l can take the values : $l=0, 1, 2$, and for an electron $s=\frac{1}{2}$, so that the multiplicity is $(2s+1)=2$.

The possible values of the inner quantum number j are $j=l\pm s$.

For $l=0$, $j=\frac{1}{2}$

For $l=1$, $j=\frac{3}{2},\frac{1}{2}$

For $l=2$, $j=\frac{5}{2},\frac{3}{2}$.

Hence, the possible terms are $^2S_{1/2}$, $^2P_{3/2}$, $^2P_{1/2}$, $^2D_{5/2}$, $^2D_{3/2}$.

For the state $^2D_{5/2}$, we have $l=2$, $s=\frac{1}{2}$, $j=\frac{5}{2}$.

Therefore, $\cos(\vec{L},\vec{S}) = \dfrac{j(j+1)-l(l+1)-s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}} = \dfrac{\frac{35}{4}-6-\frac{3}{4}}{2\sqrt{6\times\frac{3}{4}}} = 0.4714.$

Therefore, angle $(\vec{L},\vec{S}) = \cos^{-1}(0.4714) = 61.9°.$

11. Calculate possible angles between $\vec{L}$ and $\vec{S}$ for a '*d*' electron in one-electron atom.

Soln. For a '*d*' electron, we have $l = 2$ and of course $s = \frac{1}{2}$.

The two possible values of j are $j = l \pm s = \dfrac{5}{2}$ and $\dfrac{3}{2}$.

The angle between $\vec{L}$ and $\vec{S}$ is given by $\cos(\vec{L},\vec{S}) = \dfrac{j(j+1)-l(l+1)-s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$.

For $l = 2$, $s = \dfrac{1}{2}$ and $j = \dfrac{5}{2}$, we have $\cos(\vec{L},\vec{S}) = 0.4714$ (as obtained in last problem)

Therefore, angle $(\vec{L},\vec{S}) = \cos^{-1}(0.4714) = 61.9°$.

For $l = 2$, $s = \dfrac{1}{2}$ and $j = \dfrac{3}{2}$, we have $\cos(\vec{L},\vec{S}) = \dfrac{\frac{15}{4}-6-\frac{3}{4}}{2\sqrt{6}\sqrt{\frac{3}{4}}} = -\sqrt{\dfrac{1}{2}} = -0.7071.$

Therefore, angle $(\vec{L},\vec{S}) = \cos^{-1}(-0.7071) = 135°$.

The possible angles are 61.9° and 135°.

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Chapter 3

Spectroscopic Terms : L-S and J-J Couplings

Calculation of spectroscopic terms: Spectroscopic term is one, where electron in an atom is more probably live.

The spectroscopic terms are determined as

$$\boxed{n^{2s+1}L_J^P}$$

where, n is principal quantum number, s is spin quantum number, L is orbital quantum number, J is total angular quantum number and P stands for parity.

If the spectroscopic term is obtained for a system of odd electronic configurtion, we write 'O' and for even electronic configuration we don't write anything (The odd and even configuration is determined by the total l values).

If L = 0, S state ; L = 1, P state; L =2, D state etc.

Various types of coupling:

There are two types of coupling, arises due to three kind of interactions viz. spin-spin correlation, orbital-orbital interaction (residual electrostatic interaction) and spin-orbit interaction. There are

(i) L-S coupling (in lighter atoms)

(ii) j-j coupling (in heaviour atoms)

L-S coupling : Let us consider a multielectron atom (orion) having a nuclear charge + Ze, surroundings by N electrons $(N \leq Z)$. The electrons nucleus and a few of them remain in a partially-filled subshell and are optically active.

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The Hamiltonian for such an atom consists of the following terms

E =Kinetic energy of the electrons (1)

+ Electrostatic energy of the electrons with the nucleus (2)

+ Neutral electrostatic energy of electrons (3)

+ Spin-spin correlation energy (4)

+ The spin-orbit magnetic interaction energy of the electrons (5)

$$= \underbrace{\sum_{i=1}^{N} \frac{p_i^2}{2m}}_{(1)} + \underbrace{\left(-\sum_{i=1}^{N} \frac{Ze^2}{r_i} \right)}_{(2)} + \underbrace{\left(\sum_{i=1}^{N} \sum_{j=1}^{N-1} \frac{e^2}{r_{ij}} \right)}_{(3)}$$

+ spin-spin correlation energy $\left(\propto \frac{1}{r^3} \right)$ (4)

+ spin-orbit magnetic interaction energy of the electrons (5)

For most atoms, mainly the lighter ones, the residual (non-spherical) electrostatic interaction effect of the term (4) are the largest of the remaining terms ; the spin orbit magnetic interaction term (5) is considerally smaller, while the rest are negligible such atoms are governed by L-S coupling.

The L-S coupling is also known as "Russell - Saunders" coupling after the two astronomers who first used it in studing atomic spectra emitted by stars.

In the atoms which obey L-S coupling, the perturbations occur in the following order:

(i) Spin-spin correlation

(ii) Residual electrostatic interaction

(iii) Spin-orbit interaction

(i) Spin-spin correlation : As a result the individual spin angular momentum vectors of optical electrons are strongly coupled with one another to form a resultant spin angular momentum vector $\bar{s}$ of magnitude $\sqrt{s(s+1)}\,\hbar$, which is a constant of motion. Quantum number s can take the values

$$s = |s_1 + s_2 + \cdots|_{\min}; |s_1 + s_2 + \cdots|_{\min} + 1; \ldots..$$

The states with different values of s have considerable energy difference, the one of highest s being of lowest energy.

The state of largest s is of lowest energy can be understood by considering the case of two electrons. The spin corelation effect splits the unperturbed level into two : a singlet level and a triplet level. Because of the total eigenfunction being anti symmetric w.r.t. to an exchange of the electrons, the average distance between the two electrons is larger in the triplet state (parallel spins) than it is in the single state (anti parallel spins). Therefore the (positive) electrostatic repulsion energy is smaller in the triplet state than it is in the singlet state. Hence, triplet level lies deeper.

For one electron :

$S = s = \frac{1}{2}$, (no s-s coupling can take place as only single electron)

No splitting of s-level can take place, as no s-s corelation.

For two electrons :

$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2}$$

$$\therefore \quad s = |s_1 - s_2|; |s_1 - s_2| + 1, \ldots..$$

$= 0, 1$ (single triplet)

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For N-electrons : The possible value of S are

$$S = 0, 1, 2, \ldots., \frac{N}{2}; \qquad \text{for even } N$$

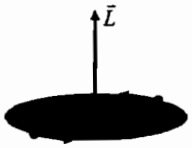
$$S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots., \frac{N}{2}; \qquad \text{for odd } N$$

(ii) Residual electrostatic interaction : As a result elecstatic interaction the orbital angular momentum vectors of "optical" electrons are strongly coupled with one another to form a resultant orbital angular momentum vector $\bar{L}$ of magnitude $\sqrt{L(L+1)}\,\hbar$ which is a constant of motion.

$$L = |\ell_1 + \ell_2 + \cdots|_{\min}; |\ell_1 + \ell_2 + \cdots|_{\min} + 1; \ldots.$$

The states with different values of L having fairly large energy differences ; the one of largest L value being of lowest energy.

Explanation : That the state of largest L is of lowest energy can be understood by considering two electrons in a Bohr atom because of the coloumb repulsion between the electrons, the electrostatic energy will be a minimum when the electrons stay at the opposite ends of a diameter, i.e. at a maximum distance apart. In this state, the two electrons would be revolving together "in the same direction" about the nucleus. i.e., with the individual orbital angular momentum vectors parallel. The magnitude of the total orbital angular momentum vector L would clearly be a maximum in this state of lowest energy.



For one electron : L-L coupling can not take place as only single electron is present. Hence, $L = \ell$ (atomic angular momentum quantum number). Note, this L will have higher value for higher energy (it does not follow the rule based on coupling as given above) as it will follow the same rule as atomic orbital quantum number.

For two electrons : $3p3d \quad \ell_1 = 1, \quad \ell_2 = 2$

$$\therefore \quad L = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1, |\ell_1 + \ell_2| = 1, 2, 3 \ (P, D, F \text{ states})$$

(iii) Spin-orbit coupling : As a result of this $\vec{L}$ and $\vec{S}$ are less strongly coupled with each other to form a vector $\vec{J}$ i.e., $\vec{J} = \vec{L} + \vec{S}$.

The coupling takes place in such way that magnitudes of $\vec{J}$, $\vec{L}$ and $\vec{S}$ remain constant.

The magnitude of $\vec{J}$ is $\sqrt{J(J+1)}\,\hbar$ where the quantum number J takes the following values

$$J = |L - S|, |L - S| + 1, \ldots, |L + S|$$

Number of multiplets $= 2S + 1$ when $L > S$

$= 2L + 1$ when $S > L$

So due to spin spin orbit coupling a level characterised by given values of L and S is farther broken up into comparatively J value. The group of these J levels forms a "fine structure multiplet".

CAREER ENDEAVOUR

Spin orbit interaction energy :

$\Delta E_{\ell s} = a(\vec{L} \cdot \vec{S})$, where a is an interaction constant.

Since, $\vec{J} = \vec{L} + \vec{S}$

Therefore, $|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2\vec{L} \cdot \vec{S}$ or $\vec{L} \cdot \vec{S} = \frac{1}{2}\left[|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2\right]$

Therefore, $\Delta E_{\ell s} = \frac{a}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\hbar^2$

Therefore, $\Delta E_{\ell s} = \alpha\left[J(J+1) - L(L+1) - S(S+1)\right]\hbar^2$

where α is another constant. However α has the same value for all the energy levels of a so called multiplet, i.e. for all the energy levels of a configuration with common values of L and S.

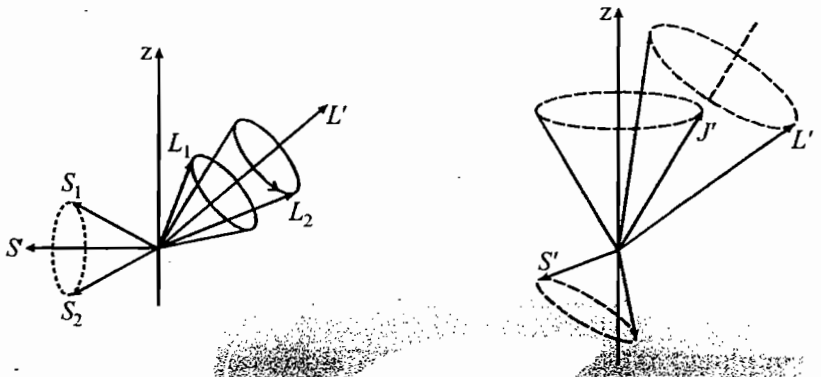
Lande's Interval Rule : It gives the relative spacing of the fine structures levels within a multiplet. If the quantum number associated with the level of lower energy is J, the quantum number associated with the level of higher energy is $J + 1$, then the separation between two fine structures levels is

$$E_{J+1} - E_J = \alpha\left[(J+1)(J+2) - L(L+1) - S(S+1)\right] - \alpha\left[J(J+1) - L(L+1) - S(S+1)\right] = 2\alpha\left[(J+1)\right]$$

Thus, the energy interval between consecutive levels J and J + 1 of a fine structure multiplet is proportional to $(J+1)$, i.e. to the largest of two J values involved. Deviations from Lande interval rule occur with increasing deviation from L - S coupling.

Vector model of L-S coupling:

The figure below illustrates the L-S coupling in the state which is normally the one of minimum energy for two optically active electrons with quantum number $\ell_1 = 1, s_1 = \frac{1}{2}$ and $\ell_2 = 2, s_2 = \frac{1}{2}$.



Here the spin angular momenta $\vec{s}_1$ and $\vec{s}_2$ precess about their sum $\vec{s}'$ and $\vec{s}'$. The precession is rapid because their coupling is relatively strong. The orbital angular momenta $\vec{L}_1$ and $\vec{L}_2$ precess rapidly about their sum $\vec{L}'$ because their coupling is also relatively strong, and $\vec{L}'$ also has its max possible magnitude (corresponding to $\ell' = 3$). In addition there is a slow precession of $\vec{s}'$ and $\vec{L}'$ about their sum $\vec{J}'$, with $\vec{J}'$ having its possible min possible magnitude (corresponding to $j' = 2$). This precession is slow because the coupling between $\vec{s}'$ and $\vec{L}'$ is relatively weak. Finally, $\vec{J}'$ can be found anywhere on a cone symmetrical about the z-axis, with its component J'_z along that axis a constant given by quantization condition

$$\boxed{J'_z = m'_j \hbar}\ ; m_j = -j', -j'+1, ..., +j'$$

CAREER ENDEAVOUR

Determination of spectral terms for L-S coupling :

Since the core electrons do not contribute to the angular momentum of the atom, we must consider only the optical electrons, i.e., electrons outside the completed subshells for computing the terms.

(a) Atoms with one optical electron : $1s$

For this, $s = \frac{1}{2}$, $\ell = 0$

Therefore, $S = s = \frac{1}{2}$, multiplicity $2s + 1 = 2$ (doublet)

$L = \ell = 0\ (s)$

$J = \ell + s = \frac{1}{2}$

Therefore, term $^2S_{1/2}$

(b) Atoms with two or more non-equivalent optical electrons :

(i) $4p\,4d$

For this, $s_1 = \frac{1}{2},\ s_2 = \frac{1}{2},\ \ell_1 = 1,\ \ell_2 = 2$

Therefore, $s = |s_1 - s_2|, |s_1 - s_2| + 1 = 0, 1$

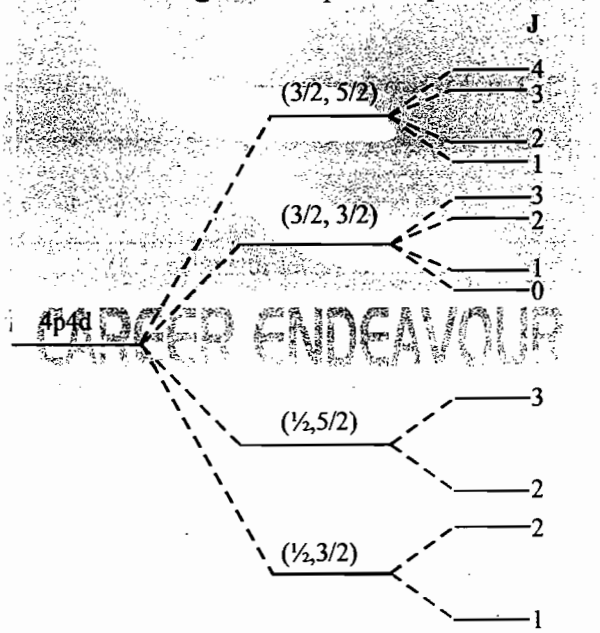
Multiplicity $(2s+1) = 1, 3$ (single, triplet)

$L = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1, ... = 1, 2, 3$ (P, D, F states)

Since, $J = |L - S|, ..., |t - s|$

Singlet terms ($s = 0$)	Triplet terms ($s = 1$)
$S=0,\ L=1$ $\Big\}$ $J=1,\ {}^1P_1$	$S=1,\ L=1$ $\Big\}$ $J=0,1,2;\ {}^3P_{0,1,2}$
$S=0,\ L=2$ $\Big\}$ $J=2,\ {}^1D_2$	$S=1,\ L=2$ $\Big\}$ $J=1,2,3;\ {}^3D_{1,2,3}$
$S=0,\ L=3$ $\Big\}$ $J=3,\ {}^1F_3$	$S=1,\ L=3$ $\Big\}$ $J=2,3,4;\ {}^3F_{2,3,4}$

Thus a single degenerate level of configuration $4p\,4d$ is splitted into 12 levels as shown below.



Unperturbed Level = Spin-orbit interaction + spin-spin correlation & residual electrostatic interaction

(ii) $3p\,4p$

For this, $\ell_1 = 1,\ s_1 = \frac{1}{2}$

and $\ell_2 = 1,\ s_2 = \frac{1}{2}$

Therefore, $S = |s_1 - s_2|,\ |s_1 - s_2| + 1 = 0, 1$

$L = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1, ... = 0, 1, 2$ (S, P, D)

Therefore, $J = |L - S|, ..., |L + S|$

Singlet terms ($s = 0$)	Triplet terms ($s = 1$)
$\left.\begin{matrix} S = 0 \\ L = 0 \end{matrix}\right\}$ $J = 0,$ $^1S_0$	$\left.\begin{matrix} S = 1 \\ L = 0 \end{matrix}\right\}$ $J = 1;$ $^3S_1$
$\left.\begin{matrix} S = 0 \\ L = 1 \end{matrix}\right\}$ $J = 1,$ $^1P_1$	$\left.\begin{matrix} S = 1 \\ L = 1 \end{matrix}\right\}$ $J = 0, 1, 2;$ $^3P_{0,1,2}$
$\left.\begin{matrix} S = 0 \\ L = 2 \end{matrix}\right\}$ $J = 2,$ $^1D_2$	$\left.\begin{matrix} S = 1 \\ L = 2 \end{matrix}\right\}$ $J = 1, 2, 3;$ $^3D_{1,2,3}$

(iii) $3d\,4s\,5p$

For this, $s_1 = \frac{1}{2},\ s_2 = \frac{1}{2},\ s_3 = \frac{1}{2}$

and $\ell_1 = 0,\ \ell_2 = 1,\ \ell_3 = 2$

Therefore, $S' = 0, 1,\ s_3 = \frac{1}{2}$

Therefore, $S = \frac{1}{2},\ \frac{1}{2},\ \frac{3}{2}$

Multiplicity $(2s + 1) = 2, 2$ and 4 (two doublet, one quartet)

$L' = |\ell_1 - \ell_3|, ..., |\ell_1 + \ell_3| = 2, 1, 3$

Therefore, $L = 1, 2, 3$

Doublet terms ($s = \frac{1}{2}$)	Quartet terms ($s = \frac{3}{2}$)
$\left.\begin{matrix} S = \frac{1}{2} \\ L = 1 \end{matrix}\right\}$ $J = \frac{1}{2}, \frac{3}{2};$ $^2P_{\frac{1}{2},\frac{3}{2}}$	$\left.\begin{matrix} S = \frac{3}{2} \\ L = 1 \end{matrix}\right\}$ $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2};$ $^4P_{\frac{1}{2},\frac{3}{2},\frac{5}{2}}$
$\left.\begin{matrix} S = \frac{1}{2} \\ L = 2 \end{matrix}\right\}$ $J = \frac{3}{2}, \frac{5}{2};$ $^2D_{\frac{3}{2},\frac{5}{2}}$	$\left.\begin{matrix} S = \frac{3}{2} \\ L = 2 \end{matrix}\right\}$ $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2};$ $^4D_{\frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2}}$
$\left.\begin{matrix} S = \frac{1}{2} \\ L = 3 \end{matrix}\right\}$ $J = \frac{5}{2}, \frac{7}{2};$ $^2F_{\frac{5}{2},\frac{7}{2}}$	$\left.\begin{matrix} S = \frac{3}{2} \\ L = 3 \end{matrix}\right\}$ $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2};$ $^4F_{\frac{3}{2},\frac{5}{2},\frac{7}{2},\frac{9}{2}}$

So terms are

$^2P_{\frac{1}{2},\frac{3}{2}}(2)$; $^2D_{\frac{3}{2},\frac{5}{2}}(2)$; $^2F_{\frac{5}{2},\frac{7}{2}}(2)$;

$^4P_{\frac{1}{2},\frac{3}{2},\frac{5}{2}}$; $^4D_{\frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2}}$; $^4F_{\frac{3}{2},\frac{5}{2},\frac{7}{2},\frac{9}{2}}$

Thus, we get a total of 23 distinct levels. In one of the quartet terms, $4p$ has three (not four) fine structure components. This is be CO_3 for this term $L = 1$ is less than $s = \frac{3}{2}$. So number of terms $= 2L + 1$.

(c) Atoms with two equivalent electrons

Equivalent electrons are those which have same value of n and ℓ.

(i) A closed subshell such as s^2, p^6, d^{10} always form a ${}^1s_0$ term only.

$$\sum m_\ell = 0 \; ; \; \sum m_s = 0$$

$\therefore \; M_L = 0 \; ; \; M_S = 0$

and so $L = 0$ (s-state) and $s = 0, J = 0$

$\therefore \; {}^1s_0$

(ii) The terms of configuration of $(n\ell)^q$ are the same as the terms of the configuration $(n\ell)^{r-q}$; where $r = 2(2\ell + 1)$

Example-1: For p^2 electrons,

$$\ell_1 = 1, \ell_2 = 1 \; ; \; m_{\ell_1} = 0, \pm 1 \; ; \; m_{\ell_2} = 0, \pm 1$$

The terms are readily calculated from Breit's scheme. In this scheme we write in a table all the possible values of $M_L (= m_{\ell_2} + m_{\ell_2})$, which can be formed by combinations of m_{ℓ_1} and m_{ℓ_2} of the two electrons.

$m_{\ell_1} =$	1	0	−1	
$M_L =$	2	1	0	1
$M_L =$	1	0	−1	0
$M_L =$	0	−1	−2	−1
				m_{ℓ_2}

There are 3 sets of M_L values :

2 1 0 −1 −2 (set-I)

1 0 −1 (set-II)

0 (set-III)

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These sets of M_L corresponds to $L = 2, 1$ and 0 respectively i.e. to one D, one P and one S term.

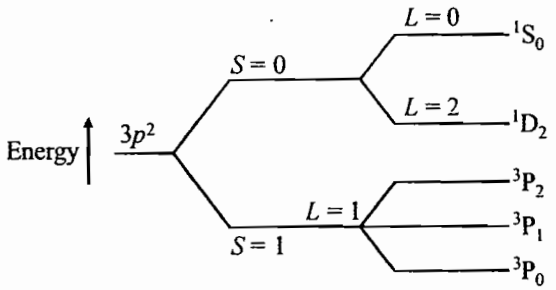
The spins of the two electrons can be combined to form either $s = 0$ (singlets) or $s = 1$ (triplets). For $s = 1$, both electrons have the same spin quantum number m_s and hence they must differ in their values of m_ℓ. We cannot, therefore combine any of the M_L values lying on the diagonal of the above table with $s = 1$ (because diagonal corresponds to equal values of m_{ℓ_1} and m_{ℓ_2}). Thus with $s = 1$; we are limited to following values of M_L.

1, 0, −1 (set-II)

which corresponds to $L = 1$ and give a $3p$ term or a ${}^3P_{0,1,2}$ multiplet ($\because \; J = 0, 1, 2$ for $L = 1$ and $s = 1$)

when $s = 0$, the electrons differ in their spin quantum numbers and there is no restriction on the values of M_L which may be combined with this values of S. Thus, the remaining sets (set-I and set-III) combine with $s = 0$ (singlet). They yield ${}^1D$ and ${}^1S$ term (for $L = 2$ and $L = 0$ respectively). Thus, terms are ${}^1S_0, {}^1D_2, {}^3P_{0,1,2}$.

Same terms for p^4 electrons.



Example-2 : For $(nd)^2$ electrons,

The Breit's scheme for possible M_L values is

m_{l_1}	2	1	0	−1	−2	
$M_L =$	4	3	2	1	0	2
$M_L =$	3	2	1	0	−1	1
$M_L =$	2	1	0	−1	−2	0
$M_L =$	1	0	−1	−2	−3	−1
$M_L =$	0	−1	−2	−3	−4	−2
						m_{l_2}

There are 5 sets of M_L values

4 3 2 1 0 −1 −2 −3 −4 (Set-I)

3 2 1 0 −1 −2 −3 (Set-II)

2 1 0 −1 −2 (Set-III)

1 0 −1 (Set-IV)

0 (Set-V)

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These sets corresponds to $L = 4, 3, 2, 1, 0$ respectively, i.e. to G, F, D, P, S forms respectively.

The spins of the two electron can be combined to form either $s = 0$ (singlets) or $s = 1$ (triplets). For $s = 1$, we are limited to M_L values from one side of the diagonal i.e. to the following sets.

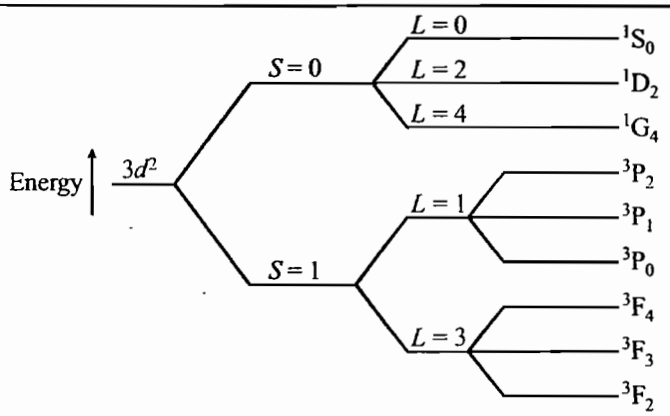
3 2 1 0 −1 −2 −3 (Set-II)

1 0 −1 (Set-IV)

These sets corresponds to $L = 3$ and $L = 1$ and give $3f$ and $3p$ terms or $^3F_{2,3,4}$ and $^3P_{0,1,2}$ multiplets. The remaining I, III and V sets of M_L values are to be combined with $s = 0$ (singlets). They yield 'G', 'D' and 'S' terms. Thus two equivalent d-electrons give

$$^1S_0,\ ^1D_2,\ ^1G_4,\ ^3P_{0,1,2},\ ^3F_{2,3,4}$$

These will also be the terms for d^8 configuration.



Example-3 : $(np)^3$ electrons

The six possible states for a single p-electron in a very strong field are

m_ℓ	=	1	0	−1	1	0	−1
m_s	=	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
		(a)	(b)	(c)	(d)	(e)	(f)

The possible states for three (equivalent) electrons $= 6c_3 = 20$.

They are

abc abd abe abf acd ace acf ade adf aef

bcd bce bcf bde bdf bef cde cdf cef def

For each of these 20 combinations we obtain $M_L = \sum m_\ell$ and $M_S (= \sum m_s)$. This gives

		abc	*abd**	*abe**	*abf**	*acd**	*ace**	*acf**	*ade**	*adf**	*aef**
m_ℓ	=	0	2	1	0	1	0	−1	2	1	0
m_s	=	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$

		bcd	*bce***	*bcf**	*bde**	*bdf***	*bef**	*cde**	*cdf***	*cef**	*def*
m_ℓ	=	0	−1	−2	1	0	−1	0	−1	−2	0
m_s	=	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

The highest values of m_ℓ are 2 which indicates a D-term $(L = 2)$. Since they occur with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$, which are the magnetic field components of $s = \frac{1}{2}$, the term is ^{2}D. A part from $m_\ell = 2$, $m_\ell = 1, 0, -1, -2$ and each with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ also belong to this term. Thus out of above 20 combinations, those marked as (*) go to form the ^{2}D term. Of the remaining terms, the highest m_ℓ are 1, and again they occur with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$. They indicate, therefore, a ^{2}P term $\left(L = 1, S = \frac{1}{2}\right)$. A part from $m_\ell = 1$, $m_\ell = 0, -1$ and each with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ also belong to this term.

Hence the combinations marked (**) belong to the ^2P term.
The remaining four combinations are

$$m_\ell = 0 \quad 0 \quad 0 \quad 0$$
$$m_s = \frac{3}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{3}{2}$$

which corresponds to $L = 0$ and $S = \frac{3}{2}$ i.e. ^4S term.

Thus the term of p^3 are $^2P_{\frac{1}{2},\frac{3}{2}}$; $^2D_{\frac{3}{2},\frac{5}{2}}$; $^4S_{\frac{3}{2}}$.

Normal and Inverted multiplets :

Within a given multiplet, usually the level with smallest J value lies lowest. Such a multiplet is a "normal" multiplet. There are however multiplets in which the largest J level lies lowest. Such multiplets are "interted" multiplets.

The reason why in a normal multiplet the smallest J level is lowest is easy to understand. The magnetic field $\vec{B}$ produced by the orbital motion of the electron in the electric field of the nucleus is in the same direction as the orbital angular momentum $\vec{L}$. In this field, the most stable state, that is the state of lowest energy must be one in which the spin magnetic moment $\vec{\mu}_s$ of the electron lines up in the direction of $\vec{B}$. We know that $\vec{\mu}_s$ is directed opposite to $\vec{s}$ because the electron is negatively charged. Thus in the lowest energy state $\vec{L}$ and $\vec{S}$ are in opposite directions and so the value of J is lowest. When $\vec{L}$ and $\vec{S}$ are in the same direction which corresponds to highest J, then $\vec{\mu}_s$ is opposite to $\vec{B}$ and the state is least stable. The inverted multiplets arise due to some perturbing influences. Usually more than half filled subshells form inverted multiplets.

Order of terms and fine structure levels :

The relative energies of the various terms and levels which arise a given electron configuration may be deduced by Hund's rule.

(i) Those with largest multiplicity lie lowest.
(ii) Of given multiplicity largest L value lies lowest. This is valid only for two or more electrons.
(ii) (a) For less than half filled subshell, the level with lowest J lies lowest (normal order).
(b) For more than half filled levels with highest J lies lowest (inverted order).

Selection rule for multi-electrons atoms in L-S coupling :

(i) No restriction on total quantum number 'n'.
(ii) For the atom as a whole, $\Delta L = 0, \pm 1$ {in one electron atom, $\Delta L \neq 0$ } and $\Delta S = 0$

$\therefore \quad \Delta J = 0, \pm 1$ {but $J = 0 \not\leftrightarrow J = 0$}

Note: The rules of L and S coupling holds only when the spin-orbit coupling is weak i.e., when the splitting between the various fine structure levels of a multiplets are very small compared to the separations between the various multiplets themselves.

The intensity rules are

(i) Those transitions are strong giving rise to intense lines in which L and J change in the same sense : the transitions are the weaker the more the change in direction of L and J is different.
(ii) A transition in the decreasing sense $(L \to L-1)$, is stronger than a transition in the increasing sense $(L \to L+1)$.

(iii) The case of oppositely directed transitions does not occur, in general either in X-ray spectra or in doublet spectra because it would lead to a final state, in which $(J \to L)$ would be 2 units greater than in the initial state, which is forbidden.

***J-J* coupling :**

In heavier atoms, spin orbit interaction term predominals over all the residual electrostatic interaction and spin-spin correlation. Here interaction between spin and angular momentum of single electron is more than interactions between spins of different electrons and orbital/angular momentum of different electrons. The perturbation takes place in following order.

(a) As a results of the stronger spin-orbit interaction, the orbitals and spin angular momentum vectors of each individual electron are strongly coupled together to form a resultant angular momentum vector j.

$$|j| = \sqrt{j(j+1)}\,\hbar \;;\; j = \ell + s \;;\; s = \frac{1}{2}$$

The unperturbed energy level is splitted into a number of well spaced levels, each corresponding to a different combination of the possible j-values for the individual valence-electrons; the lowest being the one having the smaller j-value $(j = \ell - \frac{1}{2})$.

(b) Again as a result of the residual electrostatic interaction and spin-spin interaction, the resultant angular momentum vector $\vec{j}$ of the individual electrons are less strongly coupled with one another to form the total angular momentum.

$$|j| = \sqrt{j(j+1)}\,\hbar$$

$$j = |j_1 + j_2 + j_3 + \cdots|_{\min} ; |j_1 + j_2 + \cdots|_{\min} + 1; \ldots$$

For smaller value of J, energy is lower.

Note: The above level is further splitted into a number of levels characterised by different valued of the total angular quantum number J.

Example-4 : $4p\,4d$ electrons

For the p-electrons : $\ell_1 = 1, \; s_1 = \frac{1}{2} \;\therefore\; j_1 = \left(\frac{1}{2}, \frac{3}{2}\right)$

For the d-electron : $\ell_2 = 2, \; s_2 = \frac{1}{2} \;\therefore\; j_2 = \left(\frac{3}{2}, \frac{5}{2}\right)$

This gives rise to four (j_1, j_2) combinations of the possible j_1 and j_2 values, namely

$$\left(\frac{1}{2}, \frac{3}{2}\right); \left(\frac{1}{2}, \frac{5}{2}\right); \left(\frac{3}{2}, \frac{3}{2}\right); \left(\frac{3}{2}, \frac{5}{2}\right).$$

Thus, the spin orbit effect splits the unperturbed level into four levels, of which $\left(\frac{1}{2}, \frac{3}{2}\right)$ lies lowest and $\left(\frac{3}{2}, \frac{5}{2}\right)$ highest.

The four (j_1, j_2) combinations give j-values as under :

$\left(\frac{1}{2}, \frac{3}{2}\right)$ gives $j = 1, 2$

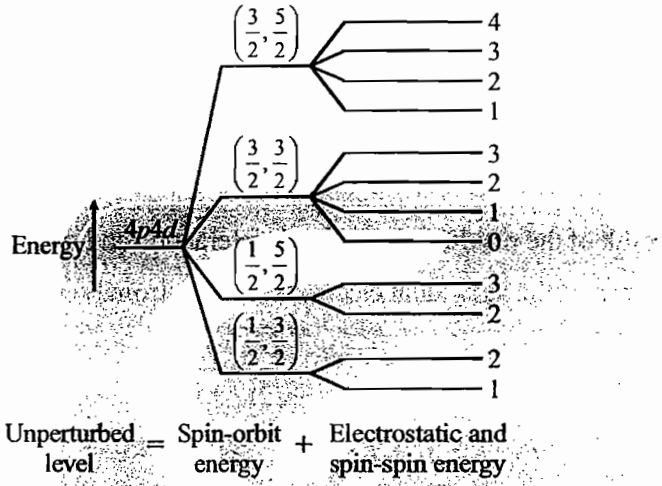
$\left(\frac{1}{2}, \frac{5}{2}\right)$ gives $j = 2, 3$

$\left(\frac{3}{2},\frac{3}{2}\right)$ gives $j=0,1,2,3$

$\left(\frac{3}{2},\frac{5}{2}\right)$ gives $j=1,2,3,4$

Hence each of the above four levels is further splitted by the electrostatic interaction and spin-spin correlation into a number of j-values, equal to the number of integrally spaced value of j that can be formed out of the two j-values.

The complete splitting is shown as :



Selection rules in j-j coupling :

$$\boxed{\Delta J=0,\pm1 \text{ (but } J=0 \not\leftrightarrow J=0)}$$

The selection rule $\Delta s=0$ and $\Delta\ell=0,\pm1$ no longer hold, since ℓ and s are no longer good quantum numbers.

(i) L-S coupling: This is also known as Russel-Saunder's coupling. This type of coupling happens in lighter atoms. In this coupling, spin-spin correlation and orbital-orbital interaction is stronger in comparision of spin-orbit interactions. It is divided into three steps:

(a) Spin-spin correlation: Due to this stronger interaction, the spin angular momentum of individual optical electrons combines to give a resultant spin angular momentum $(\vec{S})$, given as

$$\vec{S}=\vec{S}_1+\vec{S}_2+\vec{S}_3+.....$$

The magnitude of resultant spin, angular momentum $\vec{S}$ is given by $|\vec{S}|=\hbar\sqrt{s(s+1)}$

Where the total spin quantum number (s) can take the values.

$S=|s_1+s_2+....|_{min}$, $|s_1+s_2+....|_{min}+1,.....(s_1+s_2+.....)$

Example: For one electron, $S=s_1=\frac{1}{2}$ (doublet as 2s+1=2)

For two electrons, $s_1=\frac{1}{2}, s_2=\frac{1}{2}$

$\Rightarrow \quad S = |s_1 - s_2| \ldots\ldots (s_1 + s_2)$

$= 0, 1 \qquad (\text{singlet, triplets})$

For three electrons;

$s_1 = \frac{1}{2},\ s_2 = \frac{1}{2},\ s_3 = \frac{1}{2}$

$S' = 0, 1$

$S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ (Two doublets and one quartets)

In general,

1. For N even electrons $\rightarrow$ S = 0, 1, 2 .....N/2

2. For N odd electrons $\rightarrow S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots\ldots \frac{N}{2}$

OR

For one electron $\rightarrow$ $S = s_1 = 1/2$ (doublet)

For two electrons $\rightarrow$ S=0 (Singlet) S=1 (Triplet)

For three electrons $\rightarrow$ S = 1/2 (doublet) S = 1/2 (doublet) S = 3/2 (doublet)

For four electrons $\rightarrow$ S=0 (Singlet) S=1 (Triplet) S=0 (Singlet) S=1 (Triplet) S=0 (Singlet) S=1 (Triplet)

(b) Residual electrostatic interaction: As a result of this stronger interaction, the orbital angular moment of individual electrons coupled to give the resultant orbital angular momentum $\vec{L}$, given as:

$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2 + \vec{\ell}_3 + \ldots\ldots\ldots$

of magnitude given by, $|\vec{L}| = \hbar\sqrt{L(L+1)}$

Where L is known as total orbital angular momentum quantum number and it is given as

$L = \left|\vec{\ell}_1 + \vec{\ell}_2 + \ldots..\right|_{min},\ \left|\vec{\ell}_1 + \vec{\ell}_2 + \ldots..\right|_{min} + 1,\ \ldots..(\ell_1 + \ell_2 + \ldots\ldots)$

Example: For electron in 2p $\rightarrow$ $\ell_1 = 1 = L \qquad (P \text{ state})$

For electrons in 3p 3d $\rightarrow$ $\ell_1 = 1, \quad \ell_2 = 2$

$\Rightarrow \quad L = (2-1)\ldots\ldots(2+1)$

$= 1, 2, 3 \qquad (P, D, F \text{ state})$

For electrons in 2p 3p 3d → $l_1=1$ $l_2=1$ $l_3=2$

$L'=0,1,2$

$L'=0$, $l_3=2$] L=2 (D state)

$L'=1$, $l_3=2$] L=1,2,3 (P,D,F states)

$L'=2$, $l_3=2$] L=(0,1,2,3,4) (S,P,D,F,G states)

(c) Spin-orbit interaction: As a result of this week interaction, the resultant $\vec{S}$ & $\vec{L}$, couples less strongly to give total resultamt angular momentum $(\vec{J})$ given by $\vec{J}=\vec{L}+\vec{S}$ of magnitude $|\vec{J}|=\hbar\sqrt{J(J+1)}$, where total angular momentum Quantum number J is given as

$$J=|L-S|_{min} \quad |L-S|_{min}+1.....(L+S)$$

(ii) j-j coupling: This coupling is just opposite to thah of L–S coupling. It happens in heavier atoms. In it spin-orbit interaction is relatively stronger than spin-spin correlation and redisual electrostatic interaction. It happens in the following steps:

(a) Spin-orbit interaction: As a result of this relatively stronger interaction the spin angular momentum of individual electrons combine with the orbital angular momentum to give the resultant angular momentum vectors $\vec{j}_1, \vec{j}_2$.....

$\vec{j}_1=\vec{\ell}_1+\vec{s}_1, \vec{j}_2=\vec{\ell}_2+\vec{s}_2,$.....

where $|\vec{j}_1|=\hbar\sqrt{j_1(j_1+1)}$ & $j_1=\ell_1\pm s_1=\ell_1\pm\frac{1}{2}$

(b) Spin-spin correlation and residual electrostatic interaction:

As a result of these weaker interactions, $\vec{j}_1, \vec{j}_2$,..... combines to give the total resultant angular momentum $\vec{J}$ given by:

$\vec{J}=\vec{j}_1+\vec{j}_2+$.....

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of magnitude $|\vec{J}|=\hbar\sqrt{J(J+1)}$

And $J=|\vec{j}_1+\vec{j}_2+.....|_{min}, |\vec{j}_1+\vec{j}_2+.....|_{min}+1, ...(j_1+j_2+.....)$

J is total angular momentum quantum number.

Example: For 4p 4d electrons: $\ell_1=1, S_1=\frac{1}{2} \Rightarrow j_1=\frac{1}{2},\frac{3}{2}$ for p electron

$\ell_2=2, S_2=\frac{1}{2} \Rightarrow j_2=\frac{3}{2},\frac{5}{2}$ for D electron

Now (j_1, j_2) gives J

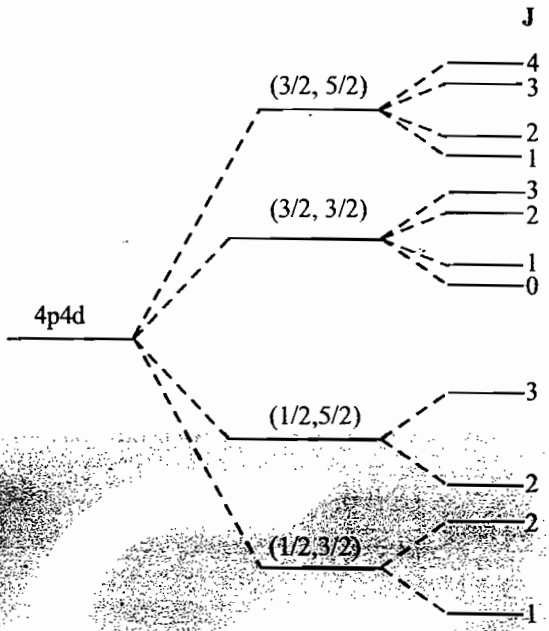
Values of j_1 & j_2 has 4 possible (j_1, j_2) combinations

$\Rightarrow$ $\left(\frac{1}{2},\frac{3}{2}\right)$ gives J=1,2

$\left(\frac{1}{2},\frac{5}{2}\right)$ gives J=2,3

$\left(\frac{3}{2},\frac{3}{2}\right)$ gives J=0,1,2,3

$\left(\frac{3}{2},\frac{5}{2}\right)$ gives J=1,2,3,4



Unperturbed Level = Spin-orbit interaction + spin-spin correlation & residual electrostatic interaction

Determination of spectral terms under L-S coupling:

Since the core electrons do not contribute to the angular momentum of the atom. We must consider only the (optical) electron outside the completed subshell for completed subshell for computing the term. We can divide the various atoms into three categories:

(i) Atom with one optical electrons:

For a hydrogen like atom ground state configuration is 1s for this we have

$\Rightarrow \quad S_1=\frac{1}{2},\ \ell_1=0$

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So, that $S=s_1=\frac{1}{2}$

Multiplicity $\left(2\times\frac{1}{2}+1\right)=2$ (doublet)

$L=\ell_1=0$ (S-slate) and $j=|L-S|,.....|L-S|+1.....(L+S)=\frac{1}{2}$

Thus the ground state term of H-atom is ${}^2S_{1/2}$. The ground state configuration of an alkali atoms Li, Na, K etc which have optical electron and electronic configuration $(n-1)s^2p^6ns^1$. The ground state term is ${}^2S_{1/2}$.

The excited state configuration and corresponding term for a H like atom would be

$2s,3s,4s.....$ ${}^2S_{1/2}$

$2p,3p,4p.....$ ${}^2p^0_{1/2}$, ${}^2p^0_{3/2}$ or ${}^2p^0_{1/2,3/2}$

$3d,4d.....$ ${}^2D_{3/2}$, ${}^2D_{5/2}$

(ii) Atoms with two or more non-equivalent optical electrons:

Let us consider an atom having optical electrons with outer configuration (2s 2p), (3s 4s) (3s, 4p) (In this, n & ℓ are not same, one of them is different or both are different).

Let us calculate terms for $\boxed{2p\,3d}$

For this we have $S_1 = \frac{1}{2}, S_2 = \frac{1}{2}, \ell_1 = 1, \ell_2 = 2$ the possible value of S & L are

$S = |S_1 - S_2|, |S_1 - S_2| + 1 \ldots\ldots (S_1 + S_2)$

$S = 0, 1$

multiplicity $= (2s+1) = 1, 3 (\text{singlet, triplet})$

and $L = |\ell_1 - \ell_2|, |\ell_1 - \ell_2| + 1 \ldots\ldots\ldots |\ell_1 + \ell_2|$

$L = 1, 2, 3 \quad (P, D, F \text{ states})$

All the terms are odd because the configuration 4p 4d is odd $(\Sigma \ell = 1 + 2 = 3)$

Now for singlets terms we have $\begin{cases} S = 0, & J = 1 \\ L = 1 \end{cases}$

$\Rightarrow$ term $^1P_1^0$

$\begin{cases} S = 0, \ j = 2 \\ L = 2 \end{cases} \Rightarrow$ term $^1D_2^0$

and $\begin{cases} S = 0, \ j = 3 \\ L = 3 \end{cases} \Rightarrow$ term $^1F_3^0$

For triplet terms, we have

$\begin{cases} S = 1, \ j = 0, 1, 2 \\ L = 1 \end{cases} \Rightarrow$ term $^3P_0^0, {}^3P_1^0, {}^3P_2^0$

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$\begin{cases} S = 1, \ j = 1, 2, 3 \\ L = 2 \end{cases} \Rightarrow$ term $3D_1^0, 3D_2^0, 3D_3^0$

$\begin{cases} S = 1, \ j = 2, 3, 4 \\ L = 3 \end{cases} \Rightarrow$ term $3F_2^0\ 3F_3^0\ 3F_4^0$

For practise, certain outer electrons configurtion and their term are given in table.

1. SS $\rightarrow$ $^1S_0, {}^3S_1$
2. SP $\rightarrow$ $^1P_1^0, {}^3P_{0,1,2}^0$
3. SD $\rightarrow$ $^1D_2, {}^3D_{1,2,3}$
4. PP $\rightarrow$ $^1S_0, {}^1P_1, {}^1D_2, {}^3S_1, {}^3P_{0,1,2}, {}^3D_{1,2,3}$

$^3D_{1,2,3}, {}^3F_{2,3,4}, {}^3G_{3,4,5}$

(i) For SS → $S_1 = \frac{1}{2}, S_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 0$

$S = 0,1$ multiplicity $(2s+1) = 1,3$ (singlet triplet)

For singlet → $s = 0, \quad J = 0$

$L = 0$

For triplet $s = 1, \quad J = 1$

$L = 0$ term ${}^3s_1$

(ii) For SP: $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 1$

$s = 0,1, \qquad j = 0,1,2$

term ${}^1p_0^1$

For triplet $s = 1 \quad J = 0,1,2$

$L = 1$ term ${}^3p_{0,1,2}^0$

(iii) For SD: $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 0, \ell_2 = 2$

$s = 0,1$

$L = 2$

For singlet $s = 0, \quad J = 2$

$L = 2$ term ${}^1D_2$

For triplet $s = 1 \quad J = 1,2,3$

$L = 2$ term ${}^3D_1, {}^3D_2, {}^3D_3$

OR

terms are ${}^1D_2, D_{1,2}$

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(iv) For PP: $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \ell_1 = 1, \ell_2 = 1$

$S = 0,1$

$L = 0,1,2$

For singlet $\begin{cases} S = 0 \\ L = 0 \end{cases}, \qquad J = 0$

term ${}^1S_0$

$\begin{cases} S = 0 \\ L = 1 \end{cases}, \qquad J = 1$ term ${}^1p_1$

$\begin{cases} S = 0 \\ L = 2 \end{cases}, \qquad J = 2$ term ${}^1D_2$

For triplet $\begin{cases} S=1 \\ L=0 \end{cases}$, $J=1$

term ${}^3S_1$

$\begin{cases} S=1 \\ L=1 \end{cases}$, $J=0,1,2$ term ${}^3p_0, {}^3p_1, {}^3p_2$

$\begin{cases} S=1 \\ L=2 \end{cases}$, $J=1,2,3$

term ${}^3D_1, {}^3D_2, {}^3D_3$

Similarly, we can determine the spectroscopic terms for three or more non-equivalent electrons.

(iii) Atoms with two or more equivalent electrons:

For two equivalent electrons (same n and l values for both or more electrons) the values atleast one of the remaining quantum numbers $(m_\ell$ or $m_s)$ must differ to satisfy Pauli exclusion principle. Hence certain terms which were possible for two or more non equivalent electrons are now not possible here. Before the determination of terms, we must discussed two important factors:

(i) A closed subshell such as s^2, p^6, d^{10}, f^{14} always form a ${}^1S_0$ term only since for them:

$\Sigma m_\ell = 0$

$\Sigma m_s = 0$

This means that $M_L = 0,\ M_s = 0$

and so, $L=0, S=0 \Rightarrow J=0 \rightarrow {}^1S_0$

(s-state) (singlet)

Therefore, J = 0, i.e. the only possible term is ${}^1S_0$. Hence, we conclude that when a subshell is completely filled the only allowed state is one in which the total spin angular momentum. Total orbital angular momentum and total angular momentum all are zero and hence no magnetic moment.

(ii) The term of configuration $(n\ell)^q$ are the same as the terms of the configuration $(n\ell)^{r-q}$ where r is the max. numbers of electrons i.e. $2(2\ell+1)$.

Example:

Terms for p^5 the same as those of $p^{6-5} = p^1$, term

Terms fo p^4 the same as those of $p^{6-4} = p^2$, the term

Terms fo d^8 the same as those of d^2 and so on.

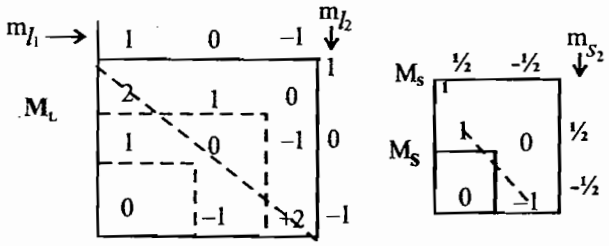
Calculation of spectroscopic term for p^2:

Here $\left.\begin{matrix} \ell_1 = 1;\ s_1 = \frac{1}{2} \\ \ell_2 = 1;\ s_2 = \frac{1}{2} \end{matrix}\right] \Rightarrow L=0,1,2 \ \&\ S=0,1$

For the calculation of spectroscopic terms in case of equivalent electrons, we have to consider the Pauli's exclusion principle i.e the four quantum number $(n, \ell, m_l$ and $m_s)$ should not be same for any two electrons in an atom. For the calculation of spectroscopic terms in case equivalent electrons we use the Breit-Scheme which is follows as:

Breit scheme for possible M_L-values is:

(i) For S =1



We take

Only L = 1

We have to leave the diagonal values for the validity. Since of Pauli's exclusion principle

$\therefore \quad J = 0,1,2$

$\therefore$ terms are ${}^3p_{0,1,2}$

(ii) For S = 0

We take the remaining L values i.e.

L = 0, 2

For L = 0, S = 0 J = 0, term is ${}^1S_0$ Parity is even, as $\Sigma\ell$ for p^2 = even

For L = 2 S = 0 J = 2 term is ${}^1D_2$

The terms for various electrons configurtion are given as:

Electonic configuration	Terms
s^1	${}^2s_{½}$
s^2, p^6, d^{10}	${}^1s_0$
p^1, p^5	${}^2p^0_{½,3/2}$
p^2, p^4	${}^1s_0,\ {}^1D_2,\ {}^3p_{0,1,2}$
p^3	${}^2p^0_{½,3/2},\ {}^2D_{½,3/2},\ {}^4s^0_{½}$
d^1, d^9	${}^2D_{½,5/2}$
d^2, d^8	${}^1S_0, {}^1D_2, {}^1G_4, {}^3P_{0,1,2}, {}^3F_{2,3,4}$

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Order of terms and fine structure levels:

The relative energies of the various terms and levels which arise from a given (equivalent) electron configuration may be deduced from a set of rules given by Hund. These rules are:

(i) Of the terms arising from equivalent electron, those with largest multiplicity (2s+1) lie lowest.

(ii) Of the terms with given multiplicity and arising from equivalent electron, that with largest L, value lies lowest.

(iii) (a) In the multiplets formed from equivalent electron in a less than half-filled subshell, the level with lowest J, lies lowest (normal order).

(b) In the multiplets formed from equivalent electron in a more than half filled subshell, the level with highest J lies lowest (inverted order)

(c) Terms arising from half filled subshell show only very slight fine structure splitting.

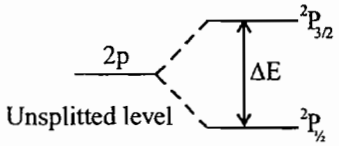
(d) The lowest terms arising from half filled subshell are the s-terms and are specially stable. These terms are ${}^2s_{1/2}$ for a half filled s-subshell, ${}^4s_{3/2}$ for a half-filled p-subshell, ${}^6s_{5/2}$ for a half filled d-subshell and ${}^8s_{7/2}$ for a half-filled f-subshell.

Hund was quite successful in predicting the lowest terms and levels of many atoms. However exceptions do occur.

Example:

Atom	Electronic configuration	Terms
${}_5B$	$1s^2, 2s^2, 2p^1$	${}^2P^0_{1/2}$ (ground), ${}^2P^0_{3/2}$
${}_6C$	$1s^2, 2s^2, 2p^2$	${}^1S_0, {}^1D_2, {}^3P_0$ (ground), ${}^3P_1, {}^3P_2$
${}_7N$	$1s^2, 2s^2, 2p^3$	${}^2p^0_{1/2}, {}^2P^0_{1/2}, {}^2D_{3/2}, {}^2D^0_{5/2}, {}^4s^0_{3/2}$ (ground)
${}_8O$	$1s^2, 2s^2 2p^4$	${}^1S_0, {}^1D_2, {}^3P_0, {}^3P_1, {}^3P_2$ (ground)
${}_9F$	$1s^2, 2s^2, 2p^5$	${}^2P^0_{1/2}, {}^2P^0_{3/2}$ (ground)
${}_{17}Cl$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	${}^2P^0_{1/2}, {}^2P^0_{3/2}$ (ground)

SPIN-ORBIT INTERACTION



Splitted due to spin orbit interaction.

The term shift in cm^{-1},

$$\Delta T = -\frac{\Delta E}{hc} = 5.84\frac{Z^4}{n^3\ell(\ell+1)}cm^{-1}$$

Or, $\Delta T \propto Z^4$.

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SOLVED PROBLEMS

1. If the doublet splitting of the first excited state, $2\,^2P_{3/2} - 2\,^2P_{1/2}$, of He^+ is $5.84\ cm^{-1}$, calculate the corresponding seperation for H.

Soln. The doublet splitting (term difference) of a one-electron atomic state arising due to spin-orbit interaction is given by

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3 \ell(\ell+1)}\ cm^{-1}$$

where, R_∞ is Rydberg constant for infinitely heavy nucleus, α is fine-structure constant and Z is atomic number.

For a given state $(n, \ell$ constant$)$, we have

$$\Delta T \propto Z^4$$

Now, for He^+, $Z = 2$ and for H, Z = 1

$$\therefore \quad \frac{\Delta T_{He^+}}{\Delta T_H} = \frac{(2)^4}{(1)^4} = 16$$

or, $$\Delta T_H = \frac{1}{16}\Delta T_{He^+} = \frac{1}{16} \times 5.84\ cm^{-1} = 0.365\ cm^{-1}$$

2. The doublet splitting of the first excited state $^2P_{3/2} - ^2P_{1/2}$ of H atom is 0.365 cm^{-1}. Calculate the corresponding separation for Li^{++}.

Soln. $\Delta T \propto Z^4$

For Li^{++} and H, Z = 3 and 1 respectively.

$$\therefore \quad \frac{\Delta T_{Li^{++}}}{\Delta T_H} = \frac{(3)^4}{(1)^4} = 8$$

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Or, $$\Delta T_{Li^{++}} = 81\,\Delta T_H = 81 \times \left(0.365\ cm^{-1}\right) = 29.6\ cm^{-1}$$

3. Calculate the spin-orbit interacting splitting of a level corresponding to n = 2 and l = 1 of Hydrogen atom.

Soln. The spin-orbit interacting splitting of an energy level is given by

$$\Delta T = 5.84 \frac{z^4}{n^3 \ell(\ell+1)}\ cm^{-1}$$

Here $n = 2$, $\ell = 1$ and $Z = 1$ (for Hydrogen atom)

$$\therefore \quad \Delta T = 5.84\left(\frac{1}{2^3 \times 1 \times 2}\right) = 0.365\ cm^{-1}$$

4. The allowed states for He($2p^2$) configuration are **[GATE 2007]**

(a) $^1S_0$, $^3S_1$, $^1P_1$, $^3P_{0,1,2}$ $^1D_2$ and $^3D_{1,2,3}$ (b) $^1S_0$, $^3P_{0,1,2}$ and $^1D_2$

(c) $^1P_1$ and $^3P_{0,1,2}$ (d) $^1S_0$ and $^1P_1$

Soln. For He ($2p^2$) configuration, we have two equivalent electrons in $2p^2$ state.

Thus, For one electron, $l_1 = 1, \quad s_1 = \frac{1}{2}$

For other electron, $l_2 = 1, \quad s_2 = \frac{1}{2}$

Thus, possible values of s and l are :

$$s = |s_1 - s_2|,\ |s_1 - s_2| + 1, \ldots, (s_1 + s_2) = \left(\frac{1}{2} - \frac{1}{2}\right),\ \left(\frac{1}{2} + \frac{1}{2}\right) = 0, 1$$

Multiplicity $(2s+1) = 1, 3$ and

$l = |l_1 - l_2|,\ |l_1 - l_2| + 1, \ldots, (l_1 + l_2) = |1-1|,\ |1-1| + 1, \ldots, (1+1) = 0, 1, 2$ (S, P, D, states)

Thus, in total we have six terms, three singlet and three triplet terms.

All these terms are even because the configuration $2p^2$ is even $(\Sigma l = 1+1 = 2)$. We can write these terms as

$^1S,\ ^1P,\ ^1D,\ ^3S,\ ^3P,\ ^3D$

To take into account spin-orbit interaction, let us combine L and S to form J.

Now, $J = |L-S|, \ldots\ldots (L+S)$.

For single terms, we have

$\begin{cases} S = 0 \\ L = 0 \end{cases}$; $J = 0$; $^1S_0$

$\begin{cases} S = 0 \\ L = 1 \end{cases}$; $J = 1$; $^1P_1$

$\begin{cases} S = 0 \\ L = 2 \end{cases}$; $J = 2$; $^1D_2$

For triplet terms, we have

$\begin{cases} S = 1 \\ L = 0 \end{cases}$; $J = 1$; $^3S_1$

$\begin{cases} S = 1 \\ L = 1 \end{cases}$; $J = 2, 1, 0$; $^3P_{0,1,2}$

$\begin{cases} S = 1 \\ L = 2 \end{cases}$; $J = 3, 2, 1$; $^3D_{1,2,3}$

For the equivalent electrons (according Hund's rule), terms $^1P_1$, $^3S_1$, $^3D_{1,2,3}$ will not be present and terms $^1S_0$, $^1D_2$, $^3P_{0,1,2}$ will be present.

Hence, correct option is (b).

5. If an atom is in the $^3D_3$ state, the angle between its orbital and spin angular momentum vectors $\left(\vec{L} \text{ and } \vec{S}\right)$ is:

[GATE 2007]

(a) $\cos^{-1}\frac{1}{\sqrt{3}}$ (b) $\cos^{-1}\frac{2}{\sqrt{3}}$ (c) $\cos^{-1}\frac{1}{2}$ (d) $\cos^{-1}\frac{\sqrt{3}}{2}$

Soln. For $^3D_3$ state, $L = 2,\ J = 3,\ 2S+1 = 3 \Rightarrow S = 1$

The angle between the orbital and spin angular momentum can be calculated using formula,

$$\cos\theta = \cos(\vec{L}\cdot\vec{S}) = \frac{-[L(L+1) + S(S+1)] + J(J+1)}{2\sqrt{L(L+1)}\cdot\sqrt{S(S+1)}}$$

$$= \frac{-[2(2+1) + 1(1+1)] + 3(3+1)}{2\sqrt{2(2+1)}\cdot\sqrt{1(1+1)}}$$

$$= \frac{-(6+2)+12}{2\times\sqrt{6}\cdot\sqrt{2}} = +\frac{4}{2\times 2\sqrt{3}} = +\frac{1}{\sqrt{3}}$$

$$\Rightarrow \quad \theta = \cos^{-1}(\vec{L}\cdot\vec{S}) = \cos\left(+\frac{1}{\sqrt{3}}\right)$$

Hence, correct option is (a).

6. In accordance with the selection rules of electric dipole transitions, the 4^3P_1 state of helium can decay by photon emission to the states **[GATE 2007]**

(a) $2^1S_0, 2^1P_1$ and 3^1D_2 (b) $3^1P_1, 3^1D_2$ and 3^1S_0

(c) $3^3P_2, 3^3D_3$ and 3^3P_0 (d) $2^3S_1, 3^3D_2$ and 3^3D_1

Soln. For Helium : $4\ ^3P_1$

For the electric dipole transition, $\Delta\ell = \pm 1$ i.e. the parity must change. Since the parities are determined by $(-1)^\ell$, the transitions corresponding to $\Delta\ell = 0, \pm 2, \pm 4, \ldots$ are not allowed, because in these cases the parities of the initial and the final eigen function would be the same. The transitions allowed by parity are $\Delta\ell = \pm 1, \pm 3, \pm 5, \ldots$

The selection rule $\Delta m_\ell = 0, \pm 1$ disallowes the transitions $\Delta\ell = \pm 3, \pm 5, \ldots$ because then Δm_ℓ may be greater than 1. Hence, the selection rule for ℓ is $\Delta\ell = \pm 1$. *Out of these four options, only option (d) corresponds to* $\Delta\ell = \pm 1$.

Hence, correct option is (d).

7. Two state of an atom have definite parities. An electric dipole transition between these states is

(a) allowed if both the states have even parities **[GATE-2010]**

(b) allowed if both the states have odd parities

(c) allowed if both the states have opposite parities

(d) not allowed unless a static electric field is applied

Soln. Electric dipole transition between two states will be allowed if both the states have opposite parities.

Hence, correct option is (c).

8. For a multielectron atom ℓ, L and S specify the one electron orbital angular momentum, total angular momentum and total spin angular momentum respectively. The selection rules for electric dipole transition between the two electronic energy levels, specified by ℓ, L and S are **[GATE-2011]**

(a) $\Delta L = 0, \pm 1;\ \Delta S = 0;\ \Delta\ell = 0, \pm 1$ (b) $\Delta L = 0, \pm 1;\ \Delta S = 0;\ \Delta\ell = \pm 1$

(c) $\Delta L = 0, \pm 1;\ \Delta S = \pm 1;\ \Delta\ell = 0, \pm 1$ (d) $\Delta L = 0, \pm 1;\ \Delta S = \pm 1;\ \Delta\ell = \pm 1$

Soln. **The selection rules for orbital angular momentum :**

For one electron the most of the transitions take place when ℓ value change by one unit, i.e., $\Delta\ell = \pm 1$ because, according to Laporte rule, the parity should be changed in a electric dipole transition. The selection rules for total orbital angular momentum.

For total angular momentum, the selection rule for the electric dipole transition is $\Delta L = 0, \pm 1$.

The selection rules for total spin angular momentum :

For total spin angular momentum, the selection rule for electric dipole transition is $\Delta S = 0$.

Hence, correct option is (b).

9. The degeneracy of an excited state of nitrogen atom having electronic configuration $1s^2\ 2s^2\ 2p^2\ 3d^1$ is

(a) 6 (b) 10 (c) 15 (d) 150 **[GATE-2011]**

Soln. For nitrogen, the electronic configuration for excited state is $1s^2\ 2s^2\ 2p^2\ 3d^1$.

For last electron, the state is $3d^1$.

For d-state, $\ell = 2$ and spin of the electron = s

Therefore, $J = (\ell + s)\ \text{to}\ |\ell - s| = \left(2 + \frac{1}{2}\right)\ \text{to}\ \left|2 - \frac{1}{2}\right| = \frac{3}{2}, \frac{5}{2}.$

Thus, degeneracy of the excited state of the nitrogen

$$= \sum_g (2J+1) = \left(2 \times \frac{3}{2} + 1\right) + \left(2 \times \frac{5}{2} + 1\right) = 4 + 6 = 10.$$

Hence, correct option is (b).

10. The terms $\{j_1, j_2\}_j$ arising from $2s^1\ 3d^1$ electronic configuration in j–j scheme are **[GATE-2012]**

(a) $\left\{\frac{1}{2}, \frac{3}{2}\right\}_{2,1}$ and $\left\{\frac{1}{2}, \frac{5}{2}\right\}_{3,2}$ (b) $\left\{\frac{1}{2}, \frac{1}{2}\right\}_{1,0}$ and $\left\{\frac{1}{2}, \frac{3}{2}\right\}_{2,1}$

(c) $\left\{\frac{1}{2}, \frac{1}{2}\right\}_{1,0}$ and $\left\{\frac{1}{2}, \frac{5}{2}\right\}_{3,2}$ (d) $\left\{\frac{3}{2}, \frac{1}{2}\right\}_{2,1}$ and $\left\{\frac{1}{2}, \frac{5}{2}\right\}_{3,2}$

Soln. The electronic configuration = $2s^1\ 3d^1$

i.e., For $2s^1$ electron : $\ell = 0,\ s = \frac{1}{2}$

For $3d^1$ electron : $\ell = 2,\ s = \frac{1}{2}$

Thus, the total angular momentum (J_1) for 2s electron

$$j_1 = [\ell + s]\ \text{to}\ |\ell - s| = \left(0 + \frac{1}{2}\right)\ \text{to}\ \left(0 - \frac{1}{2}\right) = \frac{1}{2}.$$

The total angular momentum (J_2) for $3d^1$ electron

$$j_2 = [\ell + s]\ \text{to}\ |\ell - s| = \left(2 + \frac{1}{2}\right)\ \text{to}\ \left(2 - \frac{1}{2}\right) = \frac{5}{2}, \frac{3}{2}.$$

Thus, total angular momentum J is given by

For $j_1 = \frac{1}{2}$ and $j_2 = \frac{3}{2}$: $\quad j = [j_1 + j_2]\ \text{to}\ [j_1 - j_2] = \left(\frac{1}{2} + \frac{3}{2}\right)\ \text{to}\ \left|\frac{1}{2} - \frac{3}{2}\right| = 2, 1.$

For $j_1 = \frac{1}{2}$ and $j_2 = \frac{5}{2}$: $\quad j = \left(\frac{1}{2} + \frac{5}{2}\right)\ \text{to}\ \left|\frac{1}{2} - \frac{5}{2}\right| = 2, 3.$

Thus, we can write it as $\left\{\frac{1}{2}, \frac{3}{2}\right\}_{2,1}$ and $\left\{\frac{1}{2}, \frac{5}{2}\right\}_{3,2}$

Hence, correct option is (a).

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11. The L, S and J quantum numbers corresponding to the ground state electronic configuration of boron ($z = 5$) are **[GATE-2004]**

(a) $L = 1,\ S = \frac{1}{2},\ J = \frac{3}{2}$ (b) $L = 1,\ S = \frac{1}{2},\ J = \frac{1}{2}$

(c) $L = 1,\ S = \frac{3}{2},\ J = \frac{1}{2}$ (d) $L = 0,\ S = \frac{3}{2},\ J = \frac{3}{2}$

Soln. Atomic number of boron, $z = 5$.

The electronic configuration of boron is given by $1s^2, 2s^2, 2p^1$ i.e., there is one unpaired electron in $2p$ subshell.

Thus, $l = 1,\ s = \frac{1}{2}$

According to L-S coupling, J will have values from $(l + s)$ to $|l - s|$.

Thus, $J = \left(1 + \frac{1}{2}\right)$ to $\left|1 - \frac{1}{2}\right| = \frac{3}{2}, \frac{1}{2}$.

Thus, the ground state is characterized by $L = 1,\ S = \frac{1}{2},\ J = \frac{3}{2}, \frac{1}{2}$

Hence, correct option is (b).

12. The degeneracies of the J-states arising from the ^3p term with spin-orbit interaction are **[GATE-2004]**

(a) 1, 3, 5 (b) 1, 2, 3 (c) 3, 5, 7 (d) 2, 6, 10

Soln. For the spectroscopic term ^3p we have

Multiplicity $(\delta) = 2s + 1 = 3 \Rightarrow s = \frac{1}{2},\ l = 1$

Now, for spin-orbit interaction, total angular momentum can have values from $(l + s)$ to $|l - s|$.

Thus, $J = (1 + 1)$ to $|1 - 1| = 2, 1, 0$.

So, the term is $^3p_{0,1,2}$ i.e., $^3p_0$, $^3p_1$ and $^3p_2$

Now, degeneracy of individual terms are given by

For $J = 0 \Rightarrow (2J + 1) = 1$

For $J = 1 \Rightarrow (2J + 1) = 3$

For $J = 2 \Rightarrow (2J + 1) = 5$

Hence, correct option is (a).

13. Deutron in its ground state has a total angular momentum $J = 1$ and a positive parity. The corresponding orbital angular momentum L and spin angular momentum S combination are **[GATE-2004]**

(a) $L = 0,\ S = 1$ and $L = 2,\ S = 0$ (b) $L = 0,\ S = 1$ and $L = 1,\ S = 1$

(c) $L = 0,\ S = 1$ and $L = 2,\ S = 1$ (d) $L = 1,\ S = 1$ and $L = 2,\ S = 1$

Soln. Since, the parity of any state is defined as $P = (-1)^L$, where L is orbital angular momentum of the state.

Parity will be positive if $L = 0, 2, 4, 6, \ldots$ and negative if $L = 1, 3, 5, 7, \ldots$

Now, $J = (L + S)$ to $|L - S|$

Thus, we get $J = 1$ for the following L and S combinations.

For $L = 0,\ S = 1$ and $L = 2,\ S = 1$

Hence, correct option is (c).

14. The Lande g-factor for the ${}^3p_1$ level of an atom is **[GATE-2001]**

(a) $\frac{1}{2}$ (b) $\frac{3}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$

Soln. For ${}^3p_1$ term, $l=1,\ j=1,\ 2s+1=3 \Rightarrow s=1$

Therefore, Lande g-factor

$$g=1+\left[\frac{j(j+1)-l(l+1)+s(s+1)}{2j(j+1)}\right]=1+\left[\frac{1(1+1)-1(1+1)+1(1+1)}{2\times1\times(1+1)}\right]=1+\left[\frac{2-2+2}{4}\right]=1+\frac{1}{2}=\frac{3}{2}.$$

Hence, correct option is (b).

15. The spectral term for the atom with 70% filled subshell and only $s=\frac{3}{2}$ is **[GATE-2003]**

(a) ${}^3p_0$ (b) ${}^4f_{9/2}$ (c) ${}^3f_{1/2}$ (d) ${}^4p_{1/2}$

Soln. Here, 70% filled subshell means "more than half filled subshell".

$\because \quad s=\frac{3}{2} \Rightarrow 2s+1=2\times\frac{3}{2}+1=4$

In all four options only (b) ${}^4f_{9/2}$ and (d) ${}^4p_{1/2}$ have multiplicity $(2s+1)$ equal to 4.

For ${}^4p_{1/2} \Rightarrow 2s+1=4,\ l=1$ and $J=\frac{1}{2}$

Thus, $J=(l+s)$ to $|l-s|=\left(1+\frac{3}{2}\right)$ to $\left|1-\frac{3}{2}\right|=\frac{5}{2},\frac{3}{2},\frac{1}{2}$.

For ${}^4f_{9/2} \Rightarrow 2s+1=4,\ l=3,\ J=\frac{9}{2}$

Thus, $J=(l+s)$ to $|l-s|=\left(3+\frac{3}{2}\right)$ to $\left|3-\frac{3}{2}\right|=\frac{9}{2},\frac{7}{2},\frac{5}{2},\frac{3}{2}$

Hence, the spectral term will be ${}^4f_{9/2}$

Hence, correct option is (b).

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16. The spectral terms for a certain electronic configuration are given by ${}^3d,\ {}^1d,\ {}^3p,\ {}^1p,\ {}^5s,\ {}^3s$. The term with the lowest energy is **[GATE-2004]**

(a) ${}^5s$ (b) ${}^3p$ (c) ${}^3d$ (d) ${}^3s$

Soln. Here, we have following spectral terms, ${}^3d,\ {}^1d,\ {}^3p,\ {}^1p,\ {}^5s,\ {}^3s$. The term with lowest energy will have larges value of s.

Out of the above four options only ${}^5s$ have largest value of multiplicity i.e., $2s+1=5 \Rightarrow s=2$.

Hence, correct option is (a).

17. The degeneracy of the spectral term ${}^3f$ is **[GATE-2004]**

(a) 7 (b) 9 (c) 15 (d) 21

Soln. For ${}^3f$ term; $2s+1=3 \Rightarrow s=1$ and $l=3$

Therefore, total angular momentum $J=(l+s)$ to $|l-s|=(3+1)$ to $(3-1)=4,3,2$.

Now, total number of $m_j=\sum_{J=2}^{4}(2J+1)=(2\times4+1)+(2\times3+1)+(2\times2+1)=9+7+5=21$.

Therefore, degeneracy of spectral term ^3f is 21.

Hence, correct option is (d).

18. The Lande g-factor for the level $^3d_3$ is **[GATE-2004]**

(a) $\frac{2}{3}$ (b) $\frac{3}{2}$ (c) $\frac{3}{4}$ (d) $\frac{4}{3}$

Soln. For $^3d_3$, $2s+1=3 \Rightarrow s=1$ and $l=2$ and $J=3$

Therefore, g-factor $(g)=1+\left[\frac{J(J+1)+s(s+1)-l(l+1)}{2J(J+1)}\right]$

$$=1+\left[\frac{3(3+1)+1(1+1)-2(2+1)}{2\times3\times(3+1)}\right]=1+\left[\frac{12+2-6}{24}\right]=1+\frac{1}{3}=\frac{4}{3}.$$

Hence, correct option is (d).

19. For an electron in hydrogen atom, the states are characterized by the usual quantum numbers n, l, m_l. The electric dipole transition between any two states requires that : **[GATE-2005]**

(a) $\Delta l=0,\ \Delta m_l=0,\pm1$ (b) $\Delta l=\pm1,\ \Delta m_l=\pm1,\pm2$

(c) $\Delta l=\pm1,\ \Delta m_l=0,\pm1$ (d) $\Delta l=\pm1,\ \Delta m_l=0,\pm2$

Soln. Selection rule for electric dipole transition : $\Delta l=\pm1$

i.e., parity must change during transition and $\Delta m_l=0,\pm1,\ m_l=0 \not\leftrightarrow m_l=0$ if $\Delta l=0$

Hence, correct option is (c).

20. Which of the following transitions is NOT allowed in the case of an atom, according to the electric dipole radiation selection rule? **[GATE 2016]**

(a) $2s-1s$ (b) $2p-1s$ (c) $2p-2s$ (d) $3d-2p$

Soln. For electric dipole radiation, selection rule is $\Delta\ell=\pm1$.

Here, in option 2s – 1s, we have $\Delta\ell=0$, which is forbidden.

Thus, 2s – 1s is not allowed.

Hence, correct option is (a).

21. The number of spectroscopic terms resulting from the L.S. coupling of a $3p$ electron and a $3d$ electron is **[GATE 2016]**

Soln. For 3p 3d electron

For this we have

$$s_1=\frac{1}{2},\ s_2=\frac{1}{2},\ \ell_1=1,\ \ell_2=2$$

The possible values of S and L are:

$$S=|s_1-s_2|,\ |s_1-s_2|+1,\text{-----},(s_1+s_2)$$

$$=0,1;\ \text{multiplicity}\ (2s+1)=1,3$$

and $L=|\ell_1-\ell_2|,|\ell_1-\ell_2|+1,\text{------},(\ell_1+\ell_2)$

$$=1,2,3,(\text{P, D, F, states})$$

Thus, we have in all six terms, three singlet terms and three triiplet terms. All these terms are odd because th configuration 3p3d is odd $\left(\sum \ell = 1+2=3\right)$.

We can write these terms as

$^1P, ^1D, ^1F, ^3P, ^3D, ^3F$

To take into account spin-orbit interaction, let us combine L and S to form J. Now

$$J = |L-S|, -----(L+S)$$

Fo singlet terms, we have

$$\begin{cases} S=0 \\ L=1 \end{cases}; J=1;\ ^1P_1$$

$$\begin{cases} S=0 \\ L=2 \end{cases}; J=2;\ ^1D_2$$

$$\begin{cases} S=0 \\ L=3 \end{cases}; J=3;\ ^1F_3$$

For $\begin{cases} S=0 \\ L=3 \end{cases}; J=3;\ ^1F_3$

For triplet terms, we have

$$\begin{cases} S=1 \\ L=1 \end{cases}; J=0,1,2;\ ^3P_0, ^3P_1, ^3P_2$$

$$\begin{cases} S=1 \\ L=2 \end{cases}; J=1,2,3;\ ^3D_1, ^3D_2, ^3D_3$$

$$\begin{cases} S=1 \\ L=3 \end{cases}; J=2,3,4;\ ^3F_2, ^3F_3, ^3F_4$$

Thus a single degenerate level of configuration 3P 3d is splitted into 12 levels.

Hence, correct answer is (12).

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Chapter 4

Spectra of Alkali Elements, Zeeman Effect, Paschenback Effect and Stark Effect

SPECTRA OF ALKALI ELEMENTS

Broad feature of Alkali Spectra:

After H-atom, the simplest atoms to study with regard to their spectra are the 'Alkali atoms' Li, Na, K, Rb, Cs & Fr. The experimental study of their spectra was taken up by livening, Dewar Rydberg and Bergmann spectral lines in the emission spectrum of an alkali atom formed four series a principal series of bright and most presistant lines, a sharp series of fine lines a diffuse series a comparitively broader lines and fundamental (or Bergymann) series in the infra-red region

Taking clue from of the Balmer's formula for H.

$$\boxed{\nu_m^B = \nu_\infty^B - \frac{R}{n^2}}$$

Rydberg pointed out that the alkali series could be represented by similar formula such as

(i) Principal : $\nu_m^P = \nu_\infty^P - \frac{R}{(m+p)^2}; \quad m = 2,3,4.....\infty$

(ii) Sharp : $\nu_m^s = \nu_\infty^s - \frac{R}{(m+s)^2}; \quad m = 2,3,4.....\infty$

(iii) Diffuse : $\nu_m^D = \nu_\infty^D - \frac{R}{(m+d)^2}; \quad m = 3,4,5.....\infty$

(iv) Fundamental : $\nu_m^f = \nu_m^f - \frac{R}{(m+f)^2}; \quad m = 3,4,5.....\infty$

where ν_∞^s are the wave number of convergence limits of the corresponding series and are called 'fixed terms'. In the other so clled running terms. p, s, d and f represent Rydberg corrections for the corresponding series.

Rydberg noticed the following relations among different series of the same atom. These are

(i) The sharp and diffuse series have a common convergence limit

$$\left[\nu_\infty^s = \nu_\infty^d\right]$$

(ii) The common convergence limit is equal to the first running term (with m = 2) of the principal series

$$\left[\nu_\infty^s = \nu_\infty^d = \frac{R}{(2+p)^2}\right]$$

(iii) The convergence limit of the principal series is equal to the running term (with m = 1) of the sharp series.

$$\left[\nu_{\infty}^{p} = \frac{R}{(1+s)^2} \right]$$

(iv) The convergence limit of the fundamental series is equal to the first running term (with m = 3) of the diffuse series).

$$\left[\nu_{\infty}^{f} = \frac{R}{(3+d)^2} \right]$$

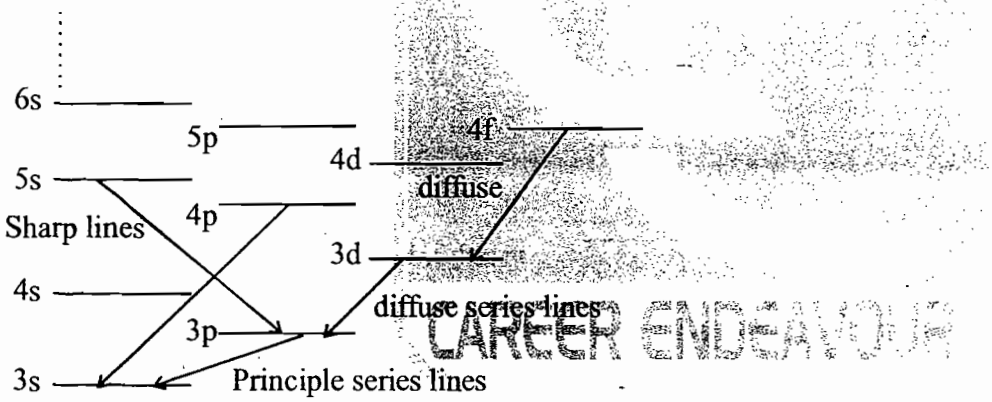
In view of these observations the above formula may be written in the following form:

(i) Principal : $\nu_m^p = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2}; \quad m = 2,3,4....\infty$

(ii) Sharp : $\nu_m^s = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2}; \quad m = 2,3,4....\infty$

(iii) Diffuse : $\nu_m^d = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2}; \quad m = 4,5....\infty$

(iv) Fundamental : $\nu_m^f = \frac{R}{(3+d)^2} - \frac{1}{(m+1)^2}; \quad m = 4,5,....\infty$



[Emission spectra of sodium]

ZEEMAN EFFECT

The splitting of spectral lines by a magnetic field is called Zeeman effect. It was discovered by Zeeman in 1896. It is a configuration of space quantisation. When an atom is placed in a magnetic field, its spectral lines further split into several polarised components. The splitting is proportional to the strength of the applied field.

(i) Normal Zeeman effect :

The normal Zeeman effect which is shown by all lines due to transitions between the singlet ($s = 0$) states of an atom, can be explained from the classical theory and also from the quantum theory without taking note of electronic spin.

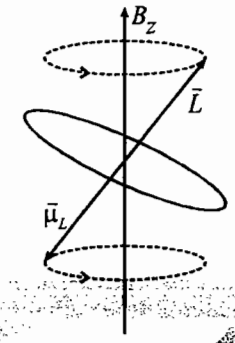
In the normal Zeeman effect a single line of wavelength λ_0 in the presence of a magnetic field is split into three components with wavelengths $\lambda_0 - \Delta\lambda$, λ_0 and $\lambda_0 + \Delta\lambda$ when viewed at right angles to the magnetic field $\vec{B}$.

The lines of wavelength $\lambda_0 + \Delta\lambda_0$ are plane-polarised with electric vector perpendicular to $\vec{B}$, while the

central line has the wavelength of the source and is plane polarized with electric vector parallel to the field $\vec{B}$. This is called a "normal triplet".

Explanation : In terms of quantum theory, a atom possess an angular polyelectronic momentum $\vec{L}$ and an orbital magnetic moment $\vec{\mu}_L$ with following relation

$$\frac{|\vec{\mu}_L|}{|\vec{L}|} = \frac{e}{2m} \; (\vec{\mu}_L \text{ is directed opposite to } \vec{L})$$



The magnetic potential energy of an atom in a magnetic field is given by

$E = -\vec{\mu}_L \cdot \vec{B} = -\mu_{L_z} B_z$ ($\because$ B is in z-direction)

$$\therefore \; E = -\left(-\frac{e}{2m} m_L \hbar\right) B_z = \left(\frac{eB\hbar}{2m}\right) m_L = m_L \left(\frac{e\hbar}{2m}\right) B \quad (\because B_z = B)$$

$\boxed{E = m_L \, \mu_B \cdot B}$, where $\mu_B = \frac{e\hbar}{2m}$ (Bohr magneton)

Because m_L can have $2L+1$ values, a state of given orbital quantum number L is split into $2L+1$ substates that differ in energy by $\mu_B \cdot B$ when the atom is in magnetic field. But the selection rules permit only.

$\boxed{\Delta m_L = 0, \pm 1}$

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So only three components

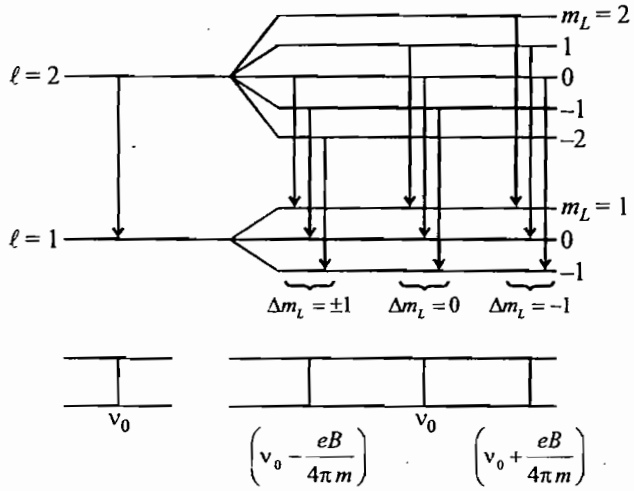
$$\boxed{\nu_i = \nu_0 - \frac{\Delta E}{h}} \quad (\Delta E = \Delta m_L \, \mu_B \cdot B)$$

Note: $\boxed{\Delta = \text{final} - \text{initial}}$

$$\nu_1 = \nu_0 - \frac{\mu_B \cdot B}{\hbar} \qquad (\text{for } \Delta m_L = \pm 1)$$

$$\nu_2 = \nu_0 \qquad (\text{for } \Delta m_L = 0)$$

$$\nu_3 = \nu_0 + \frac{\mu_B \cdot B}{h} \qquad (\text{for } \Delta m_L = -1)$$



(Spectrum without magnetic field) (Spectrum with magnetic field present)

Quantum mechanics leads not only to selection rules but also to the polarisation rules. For observation normal to the field, the transition $\Delta m_L = 0$ results in spectral line polarised with the electric vector parallel to the field (π-component) while the transition $\Delta m_L = \pm 1$ results in lines polarized with the electric vector perpendicular to the field (σ-component).

The separation of the Zeeman components is

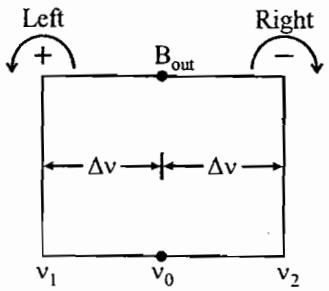
$$\boxed{\Delta\nu = \frac{eB}{4\pi m}} \text{ or } \boxed{\Delta\lambda = \frac{\lambda^2 \Delta\nu}{c} = \frac{eB\lambda^2}{4\pi mc}}$$

We can find e/m from $\boxed{\frac{e}{m} = \frac{4\pi\,\Delta\nu}{B}}$

Normal transverse Zeeman effect and longitudinal Zeeman effect.

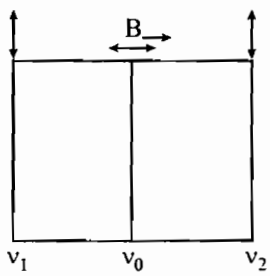
(a) Transverse Zeeman effect : when the source is viewed at right angles to magnetic field direction, it splits into three components one π and two σ. This is called transverse Zeeman effect.

(b) Longitudinal Zeeman effect : when source is viewed in the direction of the magnetic field, along the z-axis, we obtain two lines which are circularly polarized in opposite sense. It is called longitudinal Zeeman effect.



(Viewed in direction of the field $\vec{B}$)

(Longitudinal Zeeman effect)



(Viewed perpendicular to field)

(Transverse Zeeman effect)

Anomalous Zeeman Effect :

When an atom is placed in an external magnetic field and then excited, the spectral line it emits in the de-excitation process are split into several components. This is called *Anomalous Zeeman Effect.*

Under the effect of external magnetic field, the magnetic moment associated with the total angular momentum $\vec{J}$ where $(\vec{J} = \vec{L} + \vec{S})$; interacts with the external magnetic field and the degeneracy in the energy due to the quantum number J is broken.

The energy level corresponding to a particular J, splits up into $(2J+1)$ levels, and the magnitude of the splitting is given by $\Delta E = -\vec{\mu}_J \cdot \vec{B}$.

Before the advent of quantum theory, these splittings were divided into two categories : Normal and anomalous.

Normal Zeeman effect : It is a special case of anomolous Zeeman effect where the transition takes place between the singlet states only. In this case, since $s = 0$ therefore, $J = L$ and $\vec{\mu}_J$ and $\vec{J}$ are anti-parallel. This results in equispaced energy splitting and we get less number of lines compared to anomalous Zeeman effect.

The precession of component of $\vec{\mu}$ perpendicular to $\vec{J}$ averages to zero. Only the component antiparallel to $\vec{J}$ remains a constant of magnitude $|\vec{\mu}_J|$ which contributes to the magnetic moment of the atom. Thus,

$$\vec{\mu}_J = \frac{(\vec{\mu}\cdot\vec{J})}{|\vec{J}|}\frac{\vec{J}}{|\vec{J}|}$$

$$\vec{\mu}_J = -\frac{\mu_B}{\hbar}\frac{\{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})\}\vec{J}}{|\vec{J}|^2} \quad \text{[from equation (iii)]}$$

$$\text{and } \Delta E = -\vec{\mu}_J \cdot \vec{B} = +\frac{\mu_B}{\hbar}\left\{\frac{(\vec{L}+2\vec{S})\cdot(\vec{L}+\vec{S})}{|\vec{J}|^2}\right\}(\vec{J}\cdot\vec{B})$$

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$$\Delta E = \frac{\mu_B}{\hbar}\left\{\frac{L^2+2S^2+3\vec{L}\cdot\vec{S}}{|\vec{J}|^2}\right\}J_z B \quad \text{... (iv)} \quad \text{(since direction of } B \text{ is in } z\text{-direction)}$$

Since, $\vec{J} = \vec{L} + \vec{S}$ or $J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$

$$\text{or } \vec{L}\cdot\vec{S} = \frac{J^2 - L^2 - S^2}{2} \quad \text{... (v)}$$

Putting this in equation (iv), we have

$$\Delta E = \frac{\mu_B}{\hbar}\left\{L^2 + 2S^2 + \frac{3(J^2 - L^2 - S^2)}{2}\right\}\frac{J_z B}{|\vec{J}|^2}$$

$$\text{So, } \Delta E = \frac{\mu_B}{\hbar}\left\{\frac{3J^2 + S^2 - L^2}{2J^2}\right\}J_z B = \frac{\mu_B}{\hbar}\left\{1 + \frac{J^2 + S^2 - L^2}{2J^2}\right\}J_z B$$

Since, $J = \sqrt{j(j+1)}\,\hbar$, $L = \sqrt{\ell(\ell+1)}\,\hbar$, $S = \sqrt{s(s+1)}\,\hbar$ and $J_z = m_j\hbar$

Therefore, $\Delta E = \mu_B \left\{1 + \frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)}\right\} B m_j$

Therefore, $\Delta E = \mu_B B g m_j$ ... (vi)

where $g = 1 + \frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)}$ ... (vii)

This quantity g is called "Lande's g factor". We can see from the above equation (vii), that when $s = 0$, $j = \ell$ and $g = 1$ and ΔE from equation (vi) becomes $\Delta E = \mu_B B m_j$ and hence we get equal splitting proportional to m_j. While for the case $s \neq 0$, the g-factor will vary and we get unequal splittings.

Applications of Zeeman Effect:

(i) By analyzing the Zeeman splitting of the spectral lines of an atom, the spectroscopist determines the Zeeman splittings of the energy levels of the atom. These can conclusively confirm the assignment of quantum number j to each level.

(ii) The g values of the energy levels can be deduced from the splitting for a known applied field, giving information about the L and S values of the electron undergoing transitions. Overall, then the term symbols for various atomic states can be deduced by Zeeman experiments.
Much of what is known about the stars has come from measurements and analysis of optical lines spectra. The pattern of lines observed in emission spectra is used to identify the composition of stars ; the intensity of lines observed in absorption spectra is used to measure the temperatures of stellar surfaces ; the Doppler shift of the spectral lines is used to measure the velocity of stars and the Zeeman effect is used to measure the magnetic fields produced by stars. Generally polarization of spectra (σ and π) is used to separate out components.

Example: Zeeman splitting of D_1 and D_2 lines of sodium.

$^2P_{3/2} \rightarrow {}^2S_{1/2}$ D_2 line

$^2P_{1/2} \rightarrow {}^2S_{1/2}$ D_1 line

The selection rule for transitions is $\Delta m_j = 0, \pm 1$ (but not $m_j = 0$ to $m_j = 0$ if $\Delta j = 0$)

CAREER ENDEAVOUR

Terms	No. of Zeeman levels	g	$m_j(+J,...,-J)$	$\Delta E = g m_j \mu_B B (g m_j)$
$^2S_{1/2}$	2	2	$\pm\frac{1}{2}$	± 1
$^2P_{1/2}$	2	$\frac{2}{3}$	$\pm\frac{1}{2}$	$\pm\frac{1}{3}$
$^2P_{3/2}$	4	$\frac{4}{3}$	$\pm\frac{3}{2}, \pm\frac{1}{2}$	$\pm 2, \pm\frac{2}{3}$

For $\Delta m_j = 0$; components are polarised with electric vector parallel to the magnetic field (π- components

For $\Delta m_j = \pm 1$; components are polarised with electric vector parallel to the field (σ- components).

Calculation of shift in energy : Since $\Delta E = \mu_B B m_j g$

(a) For D_1 transition (i.e., $^2P_{1/2} \rightarrow {}^2S_{1/2}$)

(i) Transition line $m_j = -\frac{1}{2}$ to $m_j = \frac{1}{2}$ line (a)

$$E_2 = E_i - E_f = E_0 + \frac{2}{3}\times\left(-\frac{1}{2}\right)\mu_B B - 2\times\frac{1}{2}\mu_B B$$

$$E_1 = E_0 - \frac{4}{3}\mu_B B$$

(ii) Transition line $m_j = -\frac{1}{2}$ to $m_j = -\frac{1}{2}$ line (c)

$$E_2 = E_0 + \frac{2}{3}\times\left(-\frac{1}{2}\right)\mu_B B - 2\times\left(-\frac{1}{2}\right)\mu_B B = E_0 + \frac{2}{3}\mu_B B$$

(iii) Transition line $m_j = \frac{1}{2}$ to $m_j = \frac{1}{2}$ line (b)

$$E_3 = E_0 + \frac{2}{3}\times\frac{1}{2}\mu_B B - 2\times\left(\frac{1}{2}\right)\mu_B B$$

$$E_3 = E_0 - \frac{2}{3}\mu_B B$$

(iv) Transition line $m_j = \frac{1}{2}$ to $m_j = -\frac{1}{2}$ line (d)

$$E_4 = E_0 + \frac{2}{3}\times\frac{1}{2}\mu_B B - 2\times\left(-\frac{1}{2}\right)\mu_B B$$

$$E_4 = E_0 + \frac{4}{3}\mu_B B$$

So, energies are in the order

CAREER ENDEAVOUR

Zeeman observed the effect of external magnetic field ($\left(\sim\frac{1}{10}\text{ Tesla}\right)$ on spectrum lines and he observed that the spectrum line is splitted into a number of components. The electric vector of some of the lines is parallel to the applied magnetic field (π-component) while the electric field vector of some of the lines is transverse to the external magnetic field and are called σ-components.

PASCHEN-BACK EFFECT

When external field B is stronger than internal field then coupling between L and S partially broken and L and S independently precess about external field. Here L_z and S_z are quantized component (along field direction)of L and S.

$L_z = M_L\hbar \quad S_z = M_S\hbar$

The sum these two interaction energies is the main energy shift ΔE inperturbed energy level and

$$\Delta E = \Delta E_L + \Delta E_S = (M_L + 2M_S)\frac{eh}{4\pi mc}B$$

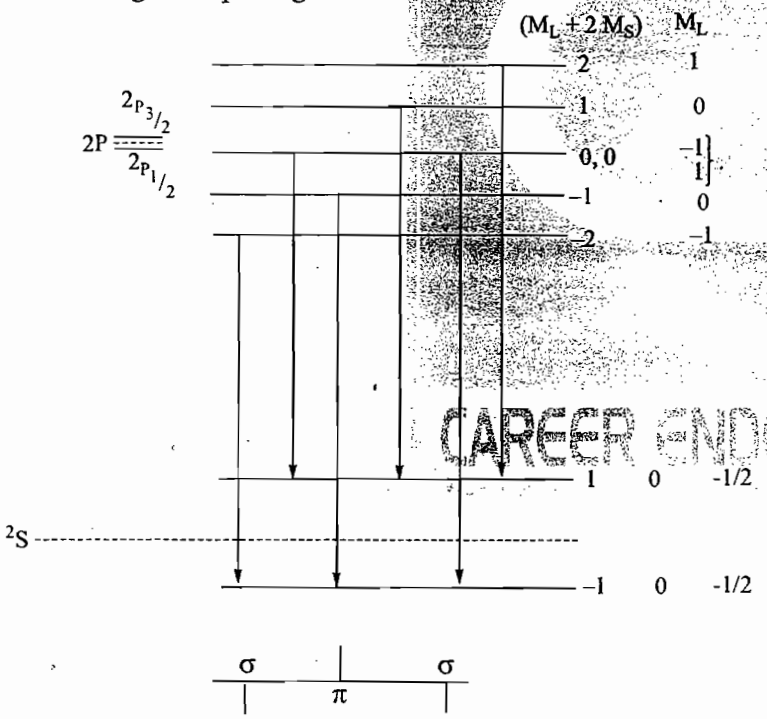
or, $-\Delta T = (M_L + 2M_S)L' \text{ cm}^{-1}$

Let us consider the transition.

$2p \rightarrow 2s$ in strong field. This transition in responsible of D_1 and D_2 lives of sodium.

Term	No. of strong-field levels $(2L+1)(2S+1)$	M_L	M_S	Shift in Lorentz unit $(M_L + 2M_S)$
^2P $\left(L=1, S=\frac{1}{2}\right)$	6	1	$\frac{1}{2}, -\frac{1}{2}$	2, 0
		0	$\frac{1}{2}, -\frac{1}{2}$	1, −1
		−1	$\frac{1}{2}, -\frac{1}{2}$	0, −2
^2S $\left(L=0, S=\frac{1}{2}\right)$	2	0	$\frac{1}{2}, -\frac{1}{2}$	1, −1

The strong field splitting of the term 2P and 2S have been shown as.



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In a strong field, the selection rules for transition are.

$\Delta M_L = 0$ (component polarised || to field)

$\Delta M_L = \pm 1$ (component polarised $\perp$ to field)

$\Delta M_S = 0$

Spin -orbit correction :

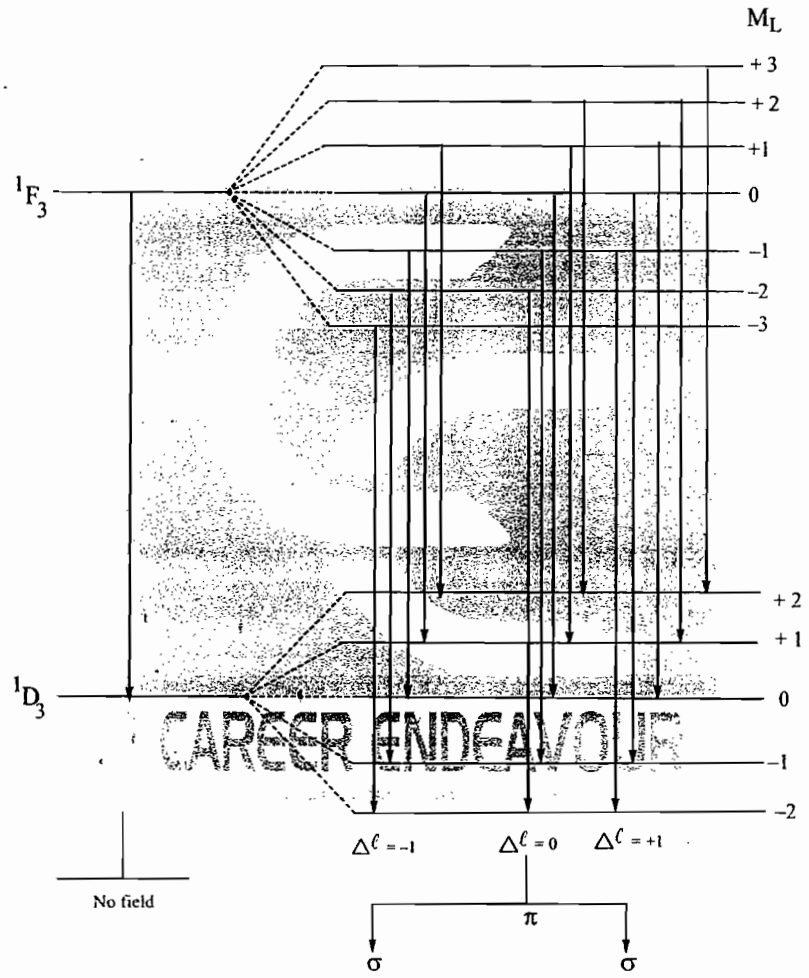
The residual spin orbit coupling changes the relative energies of the component of different term, thus $-\Delta T$ (M + $2M_S$) L' + a M_L M_S cm^{-1}. As a result of this each of the two σ component of the normal triplet splits in narrow doublets triplets according as the orginial field free transition was doublet, tripletes etc.

For intermediate field (comparable with internal field) complicated patterns are obtained.

Few examples of Zeeman effect :

(i) $^1F_3 — {}^1D_2$, it is a singlet-singlet transition and give rise to a normal Zeeman triplet.

unpertur-bed level	No. of zeeman level (2L + 1)	M_L (+L – – L)	Shift in Lorentz unit M_L
$^1F_3$	7	+3, +2, +1	3L, 2L, L
		0	0
(L = 3, S = 0, J = 3)		– 3, – 2, – 1	– 3L, – 2L, – L
$^1D_2$	5	+ 2, + 1	2L, L
(L = 2, S = 0, J = 2)		0	0
		–2, – 1	– 2L, – L



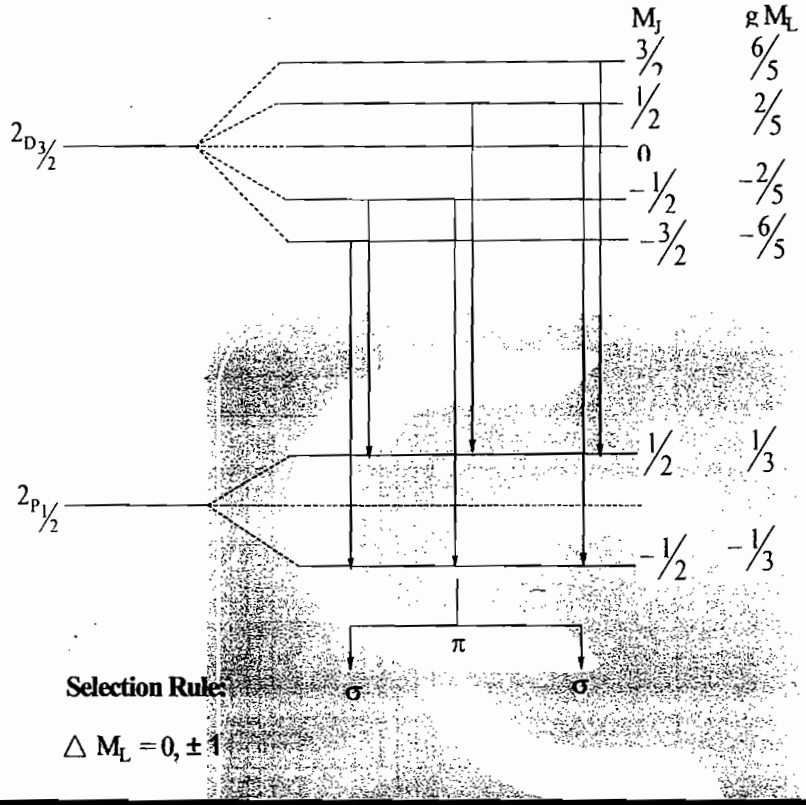
Selection Rule:

$$\boxed{\triangle M_L = 0, \pm 1}$$

(ii) $^2D_{3/2} - {}^2P_{1/2}$, It is a doublet-doublet transition so that the zeeman pattern be anomalous.

Here, $g = 1 + \dfrac{J(J+1) - L(L+1) - S(S+1)}{2J(J+1)}$

Term	No. of Zeeman (2J + 1)	g	M_J (+J, ..., J)	Shift in L' unit g M_J
$^2P_{1/2}$ (L=1, S = 1/2, J =1/2)	2	2/3	1/2 – 1/2	1/3, – 1/3
$^2D_{3/2}$ (L=2, S=1/2, J=3/2)	4	4/5	3/2 1/2 –1/2 –3/2.	6/5, 2/5, –2/5, – 6/5



Selection Rule:

$\triangle M_L = 0, \pm 1$

STARK EFFECT

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Splitting of spectrum lines in presence external electric field (F) ~ 10^5 volt/cm. It was discovered by J. Stark in 1913. There is no first order stark effect in ground state of Hydrogen atom.

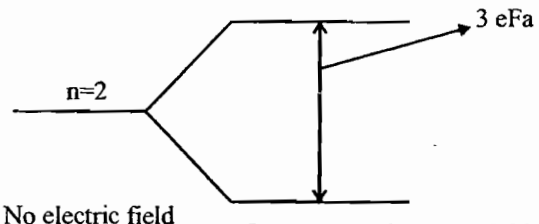
As H' = work done in electric field by electron

$$= -e\vec{F}\cdot\vec{r} = -eFr\cos\theta = \text{Perturbed Hamiltonian}$$

$$E' = \text{interaction energy} = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\psi_{100}^{*}H\psi_{100}\,d\tau, \quad \text{where } \psi_{100} = \frac{1}{\sqrt{\pi a_0}}e^{-r/a_0}$$

$$= \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\psi_{100}^{*}\left(-eFr\cos\theta\right)\psi_{100}r^2\sin\theta\,dr\,d\theta\,d\phi$$

For Hydrogen atom for first excited state n = 2.



Stark effect partially lift the degeneracy. It is of two types:

(i) Weak field Stark effect

(ii) Strong field Stark effect

Hyperfine structure of spectral lines:

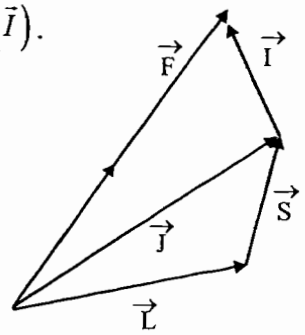
Many fine structure components of spectral lines, when examined under instruments of highest possible resolution, are further splitted into components with seperations of the order 1 cm^{-1}, which is very smaller. This is called "hyper fine structure and is explained by considering the following two factors of atomic nucleus. These are

(i) Isotope effect: (Different isotopes of an element has different mass and hence different Rydberg constant and hence energy levels.)

(ii) Nuclear spin (I): Bi(Bistmuth) has only one isotope in nature but shows six hyperfine components, thus another thing i.e. nuclear spin is also invoved in hyperfine structure.

Atomic Vector Model :

Let us now construct the vector model with nuclear spin taken into account. The total angular momentum $\left(\vec{F}\right)$ of the whole atom is the sum of three angular momenta. The electron orbital angular momentum $\left(\vec{L}\right)$, the electron spin angular momentum $\left(\vec{S}\right)$ and the nuclear spin angular momentum $\left(\vec{I}\right)$.



$\therefore \quad \vec{F} = \vec{L} + \vec{S} + \vec{I} = \vec{J} + \vec{I}$

And its magnitude $\left|\vec{F}\right| = \hbar\sqrt{F\left(F+1\right)}$, $F = \left|J - I\right|, \ldots\ldots\ldots\left(J+I\right)$

The selection rule on F are similar to that of J.

i.e. $\Delta F = 0, \pm 1$

But F = 0 $\not\leftrightarrow$ $F = 0$

Example: If $J = \frac{3}{2}$ and $I = \frac{1}{2} \Rightarrow F = 1, 2$

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Interaction Energy: The $\vec{I} - \vec{J}$ interaction energy can be shown to be given by

$$E'_{I,J} \propto \vec{I}.\vec{J}$$

$$\Rightarrow \quad E'_{I,J} = \frac{1}{2}A'\left[F\left(F+1\right) - I\left(I+1\right) - J\left(J+1\right)\right]$$

where A' is a constant. The various hfs levels of a given term of a given atom have the same I and same J, but differe in F. Hence the separation between two hfs levels can be obtained by substituting first F+I, then F, in the above equation and taking the difference. This gives

$$\Delta E' = \frac{1}{2}A'\left[\left(F+1\right)\left(F+2\right) - F\left(F+1\right)\right]$$

$$= A'\left(F+1\right)$$

Thus, the energy interval between consecutive hfs levels F and F+1 is proportion al to the larger of the F values (Lande's interval rule). The order of hfs levels in some hypermultiples is normal (smallest F level deepest) while in others it is inverted (largest F level deepest).

SOLVED PROBLEMS

1. Two levels in an atom whose nuclear spin is I = 3, have the designations $^2D_{3/2}$ and $^2P_{1/2}$. Find the expected number of components in the hyperfine structure of the corresponding spectral line.

Soln. For the state $^2D_{3/2}$, we have

$$J = \frac{3}{2}, I = 3,$$

The allowed values of the hfs quantum number F are

$$F = J + I, J + I - 1, \ldots\ldots |J - I|$$

$$= \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}.$$

Thus, for this state there are four hfs levels.

For the state $^2P_{1/2}$, we have

$$J = \frac{1}{2}, I = 3$$

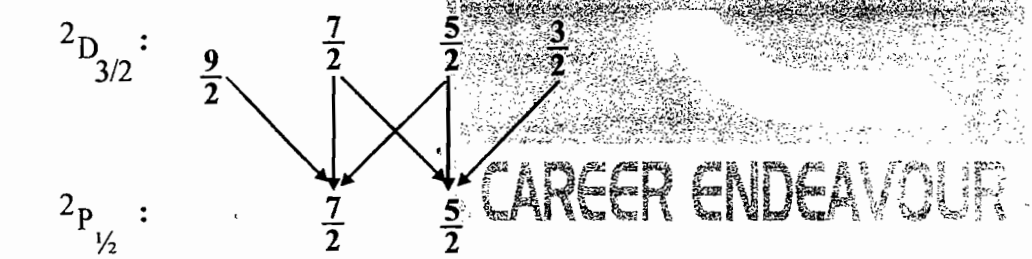
$$\therefore \quad F = \frac{7}{2}, \frac{5}{2}$$

This state has only two hfs levels.

The hfs levels combine, according to the selection rule.

$$\Delta F = 0, \pm 1$$

Hence the allowed transitions from the levels of one state to those of the other are;



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In all there are six transitions. Hence, the number of expected hfs components is 6.

2. The nuclear spin of bismuth atoms is 9/2. Using this, find the number of levels in which the term $^2D_{5/2}$ of bismuth will split due to $\vec{I} - \vec{J}$ interaction. If the separation of the $^2_2D_{5/2}$ (↓ F value) and $^2_3D_{5/2}$ levels is 30 cm^{-1}, calculate the separations of the rest of the adjacent levels.

Soln. For bismuth atom, we have $I = \frac{9}{2}$

and for its state $^2D_{5/2}$, we have $J = \frac{5}{2}$

The allowed values of the hfs quantum numer are

$$F = J + I, J + I - 1, \ldots\ldots\ldots\ldots |J - I|$$

$$= 7, 6, 5, 4, 3, 2.$$

so that there are six hfs levels, which are designated as*

$${}^2_7D_{5/2}, {}^2_6D_{5/2}, {}^2_5D_{5/2}, {}^2_3D_{5/2}, {}^2_2D_{5/2}$$

The separation between two successive levels F and F+1 is given by Lande's interval rule, that is,

$$\Delta E' = A'(F+1)$$

Therefore, as the separation between ${}^2_2D_{5/2}$ and ${}^2_3D_{5/2}$ level is 30 cm^{-1}, we have

$$30\ cm^{-1} = A'(3)$$

Or, $A' = 10\ cm^{-1}$

Hence, the separation between other levels are:

$${}^2_3D_{5/2} - {}^2_4D_{5/2} = 10\times 4 = 40\ cm^{-1}$$

$${}^2_4D_{5/2} - {}^2_6D_{5/2} = 10\times 6 = 60\ cm^{-1}$$

$${}^2_5D_{5/2} - {}^2_6D_{5/2} = 10\times 6 = 60\ cm^{-1}$$

$${}^2_6D_{5/2} - {}^2_7D_{5/2} = 10\times 7 = 70\ cm^{-1}$$

These separations have been shown in Fig.

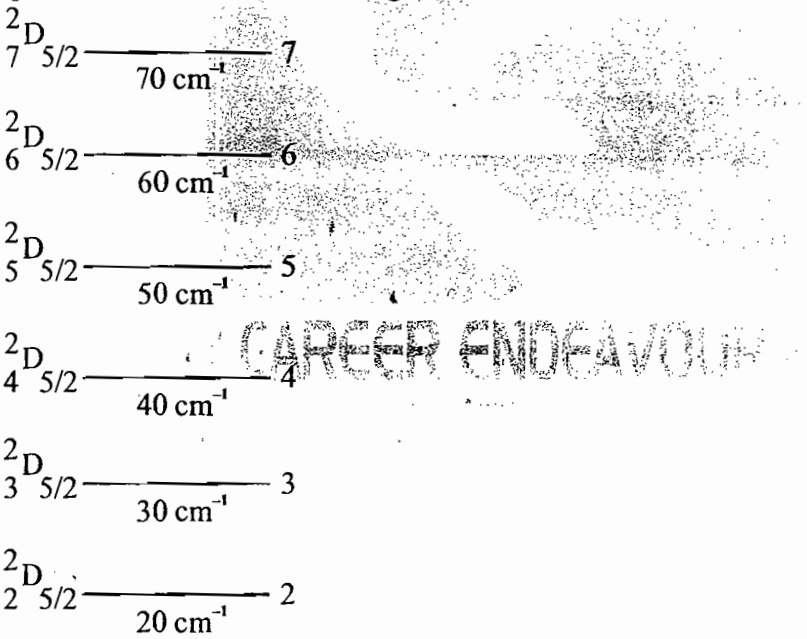


Fig.

3. The hyperfine structure of $Na\left(3^2P_{3/2}\right)$ with nuclear spin I = 3/2 has **[GATE-2007]**

(a) 1 state (b) 2 states (c) 3 states (d) 4 states

Soln. For $Na\left(3\ {}^2P_{3/2}\right)$ with nuclear spin $I = \frac{3}{2}$, we have, $J = \frac{3}{2}$, $2S+1 = 2 \Rightarrow S = \frac{1}{2}$ and $L = 1$

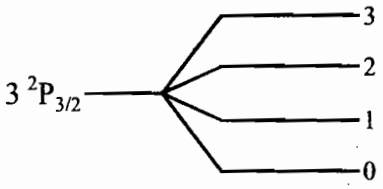
For hyperfine structure,

Total angular momentum F = total angular momentum of electron + total nuclear spin

$= (J + I), (J + I - 1), ..., (J - I)$

$\Rightarrow \vec{F} = \vec{J} + \vec{I} = \left(\frac{3}{2} + \frac{3}{2}\right)$ to $\left(\frac{3}{2} - \frac{3}{2}\right) = 3, 2, 1, 0$

Thus, we can plot this as :



Thus the hyperfine structure of Na $\left(3\ ^2P_{1/2}\right)$ with nuclear spin $I = \frac{3}{2}$ has 4 states.

4. Cesium has a nuclear spin of 7/2. The hyperfine spectrum of the D lines of the Cesium atom will consist of

(a) 10 lines (b) 4 lines (c) 6 lines (d) 14 lines **[GATE-2009]**

Soln. The nuclear spin of Cesium (I) = 7/2

For D-lines of the Cesium atom, the transitions will be from

$^2P_{3/2} \rightarrow {}^2S_{1/2}$ and $^2P_{1/2} \rightarrow {}^2S_{1/2}$

Thus, for $^2P_{3/2}$ term, we have $J = \frac{3}{2}, I = \frac{7}{2}$

Therefore, F = 5, 4, 3, 2 ...(i)

and for $^2P_{1/2}$ term, we have $J = \frac{1}{2}, I = \frac{7}{2}$

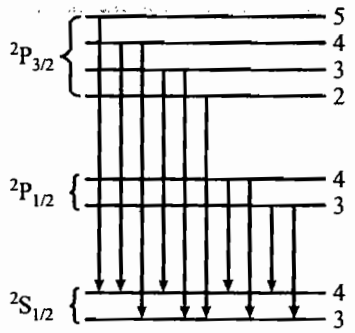
Therefore, F = 4, 3 ...(ii)

Also for $^2S_{1/2}$ term, we have $J = \frac{1}{2}, I = \frac{7}{2}$

Therefore, F = 4, 3 ...(iii)

CAREER ENDEAVOUR

Now, for hyperfine spectrum, the lines are shown with selection rule $\Delta F = 0, \pm 1$ $(0 \not\leftrightarrow 0)$



Thus, these are total 10 lines in the hyperfine spectrum.

Hence, correct option is (a).

5. Two monochromatic waves having frequencies ω and $\omega + \Delta\omega\left(\Delta\omega << \omega\right)$ and corresonding wavelength λ and $\lambda - \Delta\lambda\left(\Delta\lambda << \lambda\right)$ of same polarization, travelling along x-axis are superimposed on each other. The phase velocity and group velocity of the resultant wave are respectively given by **[GATE-2009]**

(a) $\frac{\omega\lambda}{2\pi}, \frac{\Delta\omega\lambda^2}{2\pi\Delta\lambda}$ (b) $\omega\lambda, \frac{\Delta\omega\lambda^2}{\Delta\lambda}$ (c) $\frac{\omega\Delta\lambda}{2\pi}, \frac{\Delta\omega\Delta\lambda}{2\pi}$ (d) $\omega\Delta\lambda, \omega\Delta\lambda$

Soln. The phase velocity by $v_p = \dfrac{\omega}{(2\pi/\lambda)} = \dfrac{\omega\lambda}{2\lambda}$

The group velocity is given by $v_g = \dfrac{\Delta\omega}{\Delta k} = \dfrac{\Delta\omega}{\Delta\left(\dfrac{2\pi}{\lambda}\right)} = \dfrac{\Delta\omega}{2\pi}\dfrac{\lambda^2}{\Delta\lambda}$

Hence, correct option is (a).

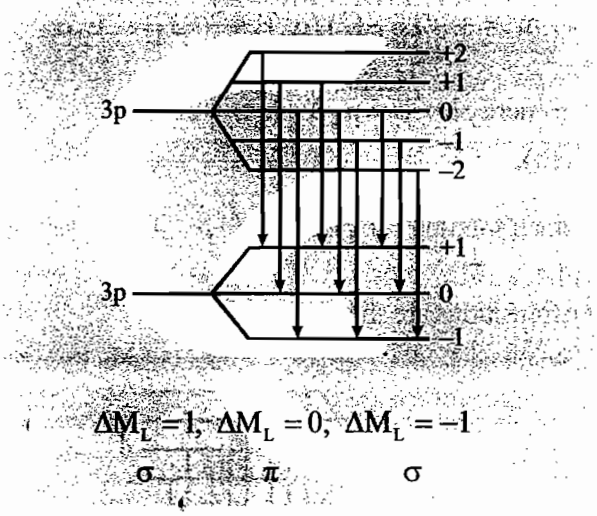
6. Consider the Zeeman splitting of a single electron system for the $3d \rightarrow 3p$ electric dipole transition. The Zeeman spectrum is : **[GATE 2009]**

(a) Randomly polarized (b) Only π polarized

(c) Only σ polarized (d) Both π and σ polarized

Soln. For $3d \rightarrow 3p$ electric dipole transition :

These terms corresponds to L = 2 to L = 1 and so, in a weak magnetic field break into 2L + 1 = 5 and 3 equispaced components respectively. The M_L values are 2, 1, 0, –1, –2 and 1, 0, –1 respectively.



The selection rule for this magnetic quantum number, as defined by quantum mechanics, is $\Delta M_L = 0, \pm 1$.

This allows nine transitions. Thus, Zeeman spectrum is both π and σ polarized.

Hence, correct option is (d).

7. An atom with one outer electron having orbital angular momentum ℓ is placed in a weak magnetic field. The number of energy levels into which the higher total angular momentum state splits, is **[GATE-2011]**

(a) $2\ell + 2$ (b) $2\ell + 1$ (c) 2ℓ (d) $2\ell - 1$

Soln. In weak field, the higher total angular momentum state splits into $(2\ell + 1)$ states.

Hence, correct option is (b).

8. The ground state of sodium atom (^{11}Na) is a $^2S_{1/2}$ state. The difference in energy levels arising in the presence of a weak external magnetic field B, given in terms of Bohr magneton, μ_B is **[GATE-2012]**

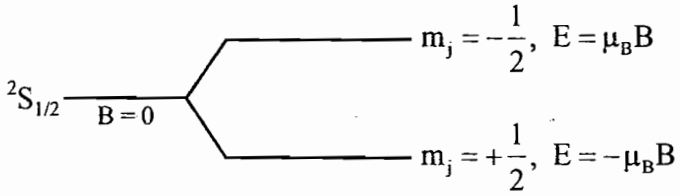
(a) $\mu_B B$ (b) $2\mu_B B$ (c) $4\mu_B B$ (d) $6\mu_B B$

Soln. For $^2S_{1/2}$ state : $\ell = 0$, $s = \dfrac{1}{2}$, $J = \dfrac{1}{2}$

For weak field, this state will split into two energy levels.

The energy of splitted energy levels is given by $E = -g\mu_B\left(\vec{J}\cdot\vec{B}\right)$

For $^2S_{1/2}$ state : $g = \dfrac{3J(J+1)-\ell(\ell+1)+s(s+1)}{2J(J+1)} = \dfrac{\left(3\times\frac{1}{2}\times\frac{3}{2}-0\times1+\frac{1}{2}\times\frac{3}{2}\right)}{\left(2\times\frac{1}{2}\times\frac{3}{2}\right)} = \dfrac{\left(\frac{9}{4}+\frac{3}{4}\right)}{\left(\frac{6}{4}\right)} = \dfrac{12}{6} = 2.$



Therefore, the energy of upper level, $\left(m_j = -\frac{1}{2}\right) = -(2)(\mu_B)\left(-\frac{1}{2}\cdot B\right) = +\mu_B B$

The energy of lower level, $\left(m_j = +\frac{1}{2}\right) = -(2)(\mu_B)\left(+\frac{1}{2}\cdot B\right) = -\mu_B B$

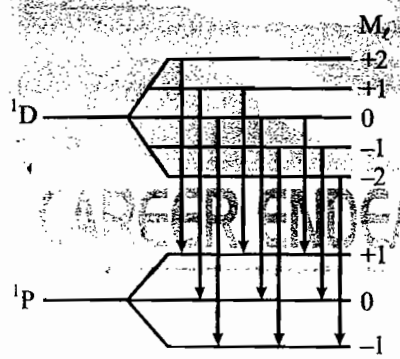
Therefore, the difference in energy levels $= \mu_B B + \mu_B B = 2\mu_B B$.

Hence, correct option is (b).

9. The number of normal Zeeman splitting components of $^1P \rightarrow {}^1D$ transition is **[GATE 2014]**

(a) 3 (b) 4 (c) 8 (d) 9

Soln. For ^{1}D to ^{1}P transition; the transitions are shown in the figure :



Selection rule; $\Delta M_\ell = 0, \pm 1$

The energy separation between two neighbouring levels in P and D states are equal.

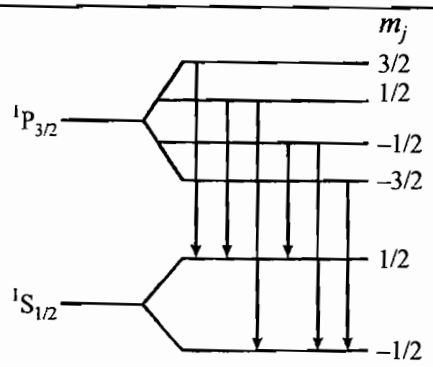
Thus, these will be only 3 normal Zeeman splitting components of $^1P \rightarrow {}^1D$ transition.

Hence, correct option is (a).

10. The number of permitted transitions from $^2P_{3/2} \rightarrow {}^2S_{1/2}$ in the presence of a weak magnetic field is_____ **[GATE 2015]**

Soln. For $^2P_{3/2} \rightarrow {}^2S_{1/2}$:

Inpresence of an external weak field, the state $^2S_{1/2}$ will split into two states $\left(m_j = \frac{1}{2}, -\frac{1}{2}\right)$ and $^2P_{3/2}$ state will split into four state $\left(m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\right)$.



Selection rule ; $\Delta m_j = 0, \pm 1,\ 0 \not\leftrightarrow 0$

Thus, there will be total six transitions permitted in $^2P_{3/2} \rightarrow {}^2S_{1/2}$.

Hence, correct answer is 6.

11. The number of hyperfine components observed in the electronic transition $^2p_{1/2} \rightarrow {}^2s_{1/2}$ of an atom with nuclear spin 1/2 is **[GATE-2001]**

(a) 3 (b) 4 (c) 6 (d) 5

Soln. For $^2p_{1/2}$ term ; $J = \frac{1}{2}$, $I = \frac{1}{2}$

The allowed value of hyperfine structure quantum number are

$F = (J+I), |J+I-1|, ..., |J-I|$

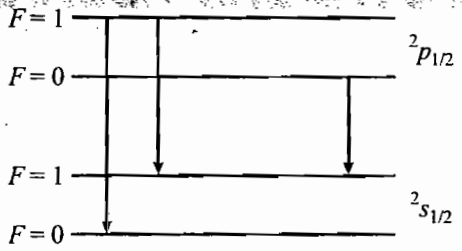
$= \left(\frac{1}{2}+\frac{1}{2}\right), \left|\frac{1}{2}+\frac{1}{2}-1\right|, ..., \left|\frac{1}{2}-\frac{1}{2}\right|$

$= 1, 0$

Similarly, for $^2s_{1/2}$ term, $J = \frac{1}{2}, I = \frac{1}{2}$

Thus, $F = 1, 0$

Now, selection rule $\Delta F = 0, \pm 1 (0 \not\leftrightarrow 0)$ will gives transitions as shown in figure.



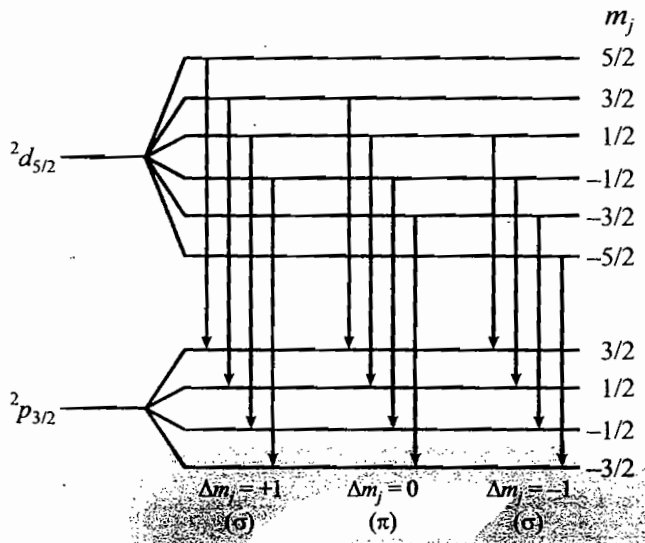
Hence, total transitions are 3.

Hence, correct option is (a).

12. The total number of Zeeman components observed in an electronic transition $^2d_{5/2} \rightarrow {}^2p_{3/2}$ of an atom in a weak field is **[GATE-2001]**

(a) 4 (b) 6 (c) 12 (d) 10

Soln. The electronic transitions of $^2d_{5/2} \rightarrow {}^2p_{3/2}$ is shown in figure (below):



The transitions with selection rules $\Delta m_j = 0, \pm 1$ gives 12 Zeeman components in a weak field.

Hence, correct option is (c).

13. The hyperfine splitting of the spectral lines of an atom is due to **[GATE-2003]**

(a) the coupling between the spins of two or more electrons

(b) the coupling between the spins of the orbital angular momentum of the electrons

(c) the coupling between the electron spin and the nuclear spin

(d) the effect of external electromagnetic fields

Soln. The hyperfine splitting of the spectral lines of an atom is due to the coupling between the electron spin and the nuclear spin.

Hence, correct option is (c).

CAREER ENDEAVOUR

14. If the quantum of state for a gas with internal energy u is $pV = \frac{-u}{3}$, then the equation for an adiabatic process is **[GATE-2005]**

(a) $pV^{1/3} = \text{constant}$ (b) $pV^{2/3} = \text{constant}$ (c) $pV^{4/3} = \text{constant}$ (d) $pV^{3/5} = \text{constant}$

Soln. For an adiabatic process $\Delta Q = 0$

Equation of state, $pV = \frac{1}{3}u$

For the radiation process, the internal energy can be given as ; $u = uV$, where V is the volume and u is the energy density.

Now, from first law of thermodynamics :

$$dQ = dU + pdV$$

$$\Rightarrow \quad 0 = d(uV) + \frac{u}{3}dV \qquad [dQ = 0 \text{ for adiabatic process}]$$

$$\Rightarrow \quad Vdu + udV + \frac{u}{3}dV = 0$$

$$\Rightarrow \quad Vdu = -\frac{4}{3}udV$$

$$\Rightarrow \quad \frac{du}{u} = -\frac{4}{3}\frac{dV}{V}$$

On integration both sides, we get

$$\ln u = -\frac{4}{3}\ln V + \ln K' \text{ ; where } \ln K' \text{ is constant of integration.}$$

$$\Rightarrow \quad \ln u = -\ln V^{4/3} + \ln K'$$

$$\Rightarrow \quad \ln\left(\frac{u}{V^{4/3}}\right) = \ln K' \Rightarrow uV^{4/3} = K'$$

$$\Rightarrow \quad CT^4V^{4/3} = K' \qquad \left[\because \text{ By stefan's law ; } u = CT^4\right]$$

$$\Rightarrow \quad T^4V^{4/3} = \frac{K'}{C}$$

$$\Rightarrow \quad TV^{1/3} = \left(\frac{K'}{C}\right)^{1/4}$$

$$\Rightarrow \quad TV^{1/3} = K'' \qquad \left[\text{Let } K'' = \left(\frac{K'}{C}\right)^{1/4}\right]$$

$$\Rightarrow \quad \left(\frac{pV}{R}\right)V^{1/3} = K''$$

$$\Rightarrow \quad pV^{4/3} = RK''$$

$$\Rightarrow \quad pV^{4/3} = K \qquad [\text{Let } RK'' = K \text{ (another constant)}]$$

Hence, correct option is (c).

CAREER ENDEAVOUR

15. The principal series of spectral lines of lithium is obtained by transitions between **[GATE-2006]**

(a) ns and $2p$, $n > 2$ (b) nd and $2p$, $n > 2$ (c) np and $2s$, $n > 2$ (d) nf and $3d$, $n > 3$

Soln. The principal series of spectral lines of lithium is obtained by transition between np to $2s$ transitions (for $n > 2$).

Hence, correct option is (c).

16. In a two electron atomic system having orbital and spin angular momenta ℓ_1, ℓ_2 and s_1, s_2 respectively, the coupling strengths are defined as $\Gamma_{\ell_1\ell_2}$, $\Gamma_{s_1s_2}$, $\Gamma_{\ell_1s_1}$, $\Gamma_{\ell_2s_2}$, $\Gamma_{\ell_1s_2}$ and $\Gamma_{\ell_2s_1}$. For the j – j coupling scheme to be applicable, the coupling strength must satisfy the condition **[GATE - 2005]**

(a) $\Gamma_{\ell_1\ell_2} \cdot \Gamma_{s_1s_2} > \Gamma_{\ell_1s_1} \cdot \Gamma_{\ell_2s_2}$ (b) $\Gamma_{\ell_1s_2} \cdot \Gamma_{\ell_2s_2} > \Gamma_{\ell_1\ell_2} \cdot \Gamma_{s_1s_2}$

(c) $\Gamma_{\ell_1s_2} \cdot \Gamma_{\ell_2s_1} > \Gamma_{\ell_1\ell_2} \cdot \Gamma_{s_1s_2}$ (d) $\Gamma_{\ell_1s_2} \cdot \Gamma_{\ell_2s_1} > \Gamma_{\ell_1s_1} \cdot \Gamma_{\ell_2s_2}$

Soln. Out of above options, only (b) $\Gamma_{\ell_1s_2} \cdot \Gamma_{\ell_2s_2} > \Gamma_{\ell_1\ell_2} \cdot \Gamma_{s_1s_2}$ is valid.

Hence, correct option is (b).

17. In the linear Stark effect, the application of an electric field **[GATE - 2006]**

(a) completely lifts the degeneracy of $n = 2$ level on hydrogen atom and splits $n = 2$ level into four levels.

(b) partially lifts the degeneracy of $n = 2$ level on hydrogen atom and splits $n = 2$ level into three levels.

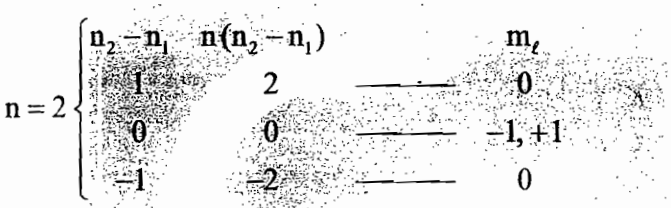
(c) partially lifts the degeneracy of $n = 2$ level on hydrogen atom and splits $n = 2$ level into two levels.

(d) does not affect the $n = 2$ levels.

Soln. For $n = 2$ level, the allowed values of n, n_1, n_2 and m_ℓ are given in following table :

n	n_2	n_1	$(n_2 - n_1)$	$2(n_2 - n_1)$	$m_\ell = [n - n_2 - n_1 - 1]$
2	1	1	0	0	-1
	1	0	1	2	0
	0	1	-1	-2	0
	0	0	0	0	1

The Stark shift of hydrogen $n = 2$ energy level is shown below :



From above figure, it is clear that two levels corresponding to $m_\ell = -1$ and $m_\ell = +1$ falls together i.e. application of electric field partially lifts the degeneracy of $n = 2$ level and splits $n = 2$ into three levels.

Hence, correct option is (b).

18. In hyperfine interaction, these is coupling between the electron angular momentum $\vec{J}$ and nuclear angular momentum $\vec{I}$, forming resultant angular momentum $\vec{F}$. The selection rules for the corresponding quantum number F in hyperfine transitions are: **[GATE - 2006]**

(a) $\Delta F = \pm 2$ only (b) $\Delta F = \pm 1$ only (c) $\Delta F = 0, \pm 1$ (d) $\Delta F = \pm 1, \pm 2$

Soln. The selection rule for the quantum number F in hyperfine transitions : $\Delta F = 0, \pm 1$ but $F = 0 \not\leftrightarrow F = 0$.

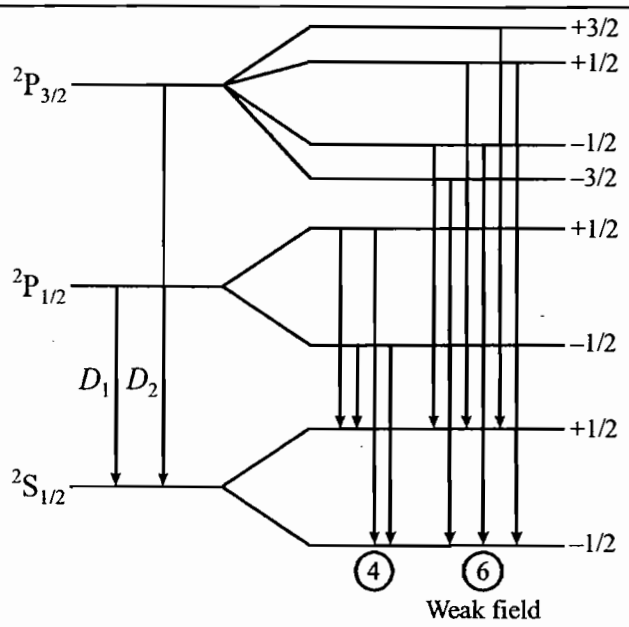
Hence, correct option is (c).

19. The D_1 and D_2 lines of Na $\left(3^2 p_{1/2} \to 3^2 s_{1/2}, 3^2 p_{3/2} \to 3^2 s_{1/2}\right)$ will split on the application of a weak magnetic field into **[GATE-2007]**

(a) 4 and 6 lines respectively (b) 3 lines each

(c) 6 and 4 lines respectively (d) 6 lines each

Soln. For weak magnetic field, D_1 and D_2 lines of Na $\left(3\,^2P_{1/2} \to 3\,^2S_{1/2},\ 3\,^2P_{3/2} \to 3\,^2S_{1/2}\right)$ will split into 4 and 6 lines respectively.



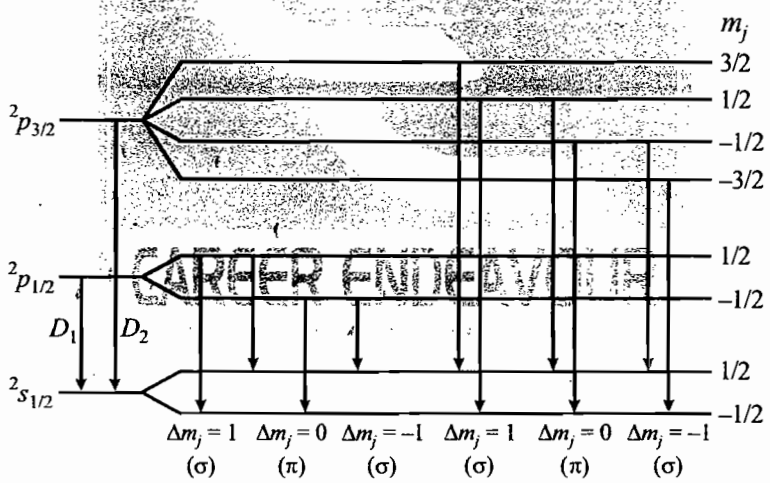
Selection rule $\Delta M_j = 0, \pm 1 \ (0 \not\leftrightarrow 0)$

Hence, correct option is (a).

20. The sodium doublet lines are due to transitions from $^2p_{3/2}$ and $^2p_{1/2}$ levels to $^2s_{1/2}$ level. On application of a weak magnetic field, the total number of allowed transitions becomes **[GATE-2005]**

(a) 4 (b) 6 (c) 8 (d) 10

Soln.



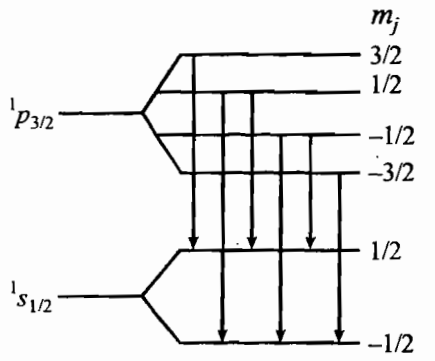
For sodium doublet lines, the total number of transitions from $^2p_{3/2}$ and $^2p_{1/2}$ levels to $^2s_{1/2}$ level is 10.

Hence, correct option is (d).

21. Assuming that the *L-S* coupling scheme is valid the number of permitted transitions from $^2p_{3/2}$ to $^2s_{1/2}$ due to a weak magnetic field is **[GATE-2004]**

(a) 2 (b) 4 (c) 6 (d) 10

Soln.



$\Delta m_j = 1,\ \Delta m_j = 0,\ \Delta m_j = -1$

(σ) (π) (σ)

According to selection rule, $\Delta m_j = 0, \pm 1 (0 \not\leftrightarrow 0)$, total number of permitted transitions from $^2p_{3/2}$ to $^2s_{1/2}$ due to a weak magnetic field is 6.

Hence, correct option is (c).

CAREER ENDEAVOUR

Chapter 5

X-Ray Spectra and The Breadth of Spectral Lines

X-RAY SPECTRA

X-rays: X-rays was discovered by Rontgen in 1896. Rontgen got nobel prize for the discovery of X-rays in 1901. He was the first physicist to get the noble prize for discovery of X-rays. X-rays are high energy photons. The wavelength of X-rays lie between 1Å to 100Å. The energy of X-rays are given by

$$E = h\nu$$
$$= h\frac{c}{\lambda}$$

Types of X-rays:

X-rays can be divided on the basis of energy and on the basis of spectrum shown.

(i) On the basis of energy: On the basis of energy X-rays are of two types:

(a) Soft X-rays: These are the X-rays of low energy. The wavelength of soft X-rays lies between 4Å to 100Å.

(b) Hard X-rays: These are the X-rays of high energy. The wavelength of hard X-rays lies between 1Å to 4Å.

(ii) On the basis of spectrum shown: On the basis of spectrum shown X-rays are divided into two parts:

(a) Continuous X-rays: It contains all possible wavelengths between 1Å to 100Å. The wavelength λ depends on applied voltage (V).

(b) Characteristic X-rays: It contains only certain wavelengths which are the characteristic of the target material i.e. λ depends on Z (atomic number).

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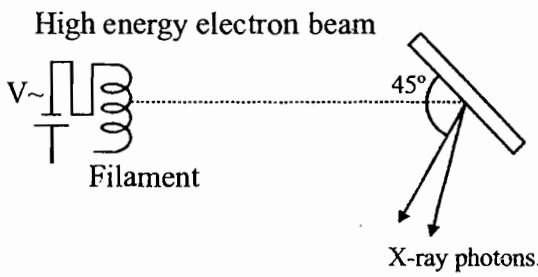
Production of X-rays:

X-rays are produced, when a high energy electron beam strikes to a heavy target (such as Molybdenum, Tungsten). The target is placed at an angle of 45° with the direction of incident electron beam. The melting point of the target should be high, so that it doesn't get melt by the high energy electrons.

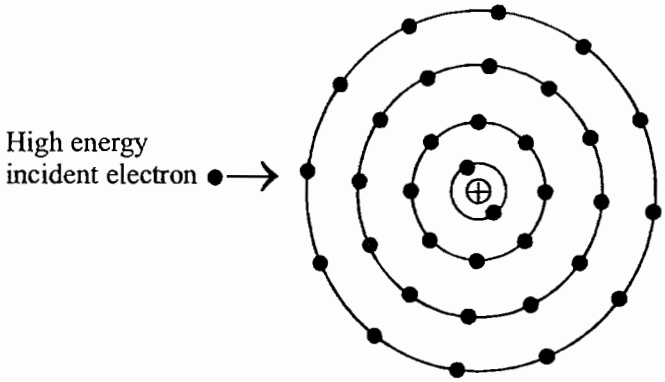


[Production of X-rays by modern cooledge tube]

The production of X-rays is based upon inverse photo-electric effect. Only 1% electron are responsible for the production of X-rays.

Mechanism of production of continuous X-Rays:

When electron of high energy are incident on a heavy material, then electron gets accelerated or deaccelerated by the nucleus and other electrons of the atoms of the material.



The electromagnetic theory says that when a charge particle gets accelerated or deaccelerated, it radiates energy. The energy radiated by the electron in such procss comes out as continuous X-rays. This is called Bremstrahlung radiation.

Thus, the maximum energy lost by electron = Max. energy of X-ray photon.

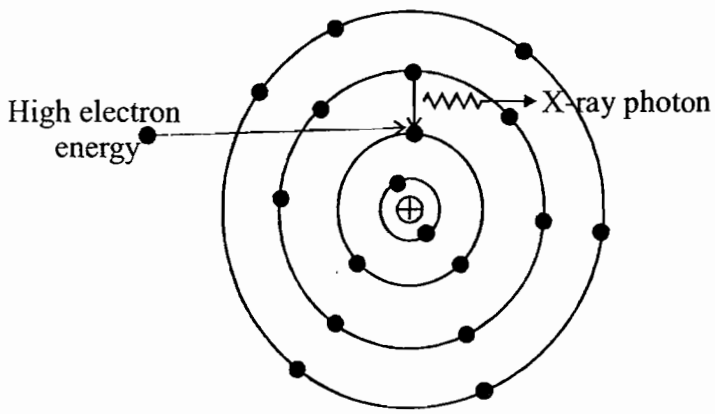
$$\Rightarrow \quad eV = \frac{hc}{\lambda_{min}}$$

$$\Rightarrow \quad \boxed{\lambda_{min} = \frac{hc}{eV} = \frac{12375}{V}\,\text{Å}} \qquad \ldots (1)$$

Equation (1) is called Duane-Hunt law. This equation gives the minimum wavelength of emitted X-rays photon. For X-rays V should be in kilovolt.

Mechanism of production of characteristic X-rays:

When high energy incident electron strikes to any of the atomic electron and electron is displaced from its orbit. So, the electron from outer orbit jump to the lower orbit just to fill the vacancy. Thus a photon of energy equal to the energy difference between two energy levels comes out. This photon is in the form of characteristic X-rays. Thus the energy of the characteristic X-ray photon is $\frac{hc}{\lambda} = E_i - E_f$.



$$\Rightarrow \quad \frac{hc}{\lambda} = -\frac{R(Z-\sigma)^2 hc}{n_i^2} - \left(-\frac{Rhc(Z-\sigma)^2}{n_f^2}\right)$$

$$\Rightarrow \quad \boxed{\frac{1}{\lambda} = R(Z-\sigma)^2\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]}$$

Where, Z is atomic number of the target and σ is screening constant.
Thus, here we also get a series of X-ray lines.

K-series characteristic X-rays:

If $n_f = 1$ and $n_i = 2,3,4.....\infty$. We get K-series lines. For K-series lines $\sigma = 1$.

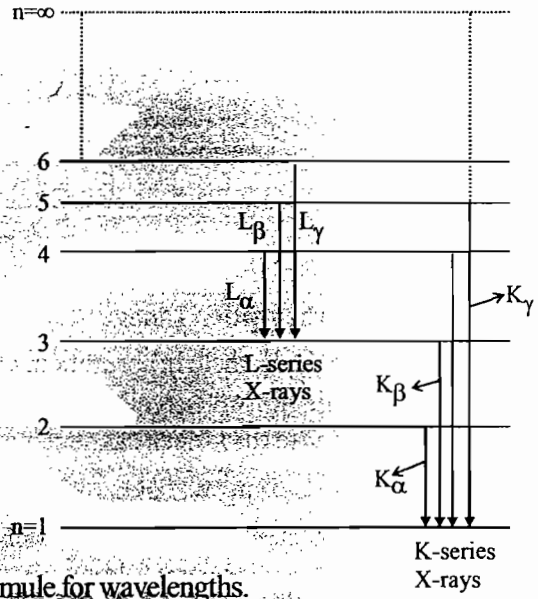
$\therefore$ Wavelength of K_α, K_β, K_r ..... lines are

$$\frac{1}{\lambda_{K_\alpha}} = R(Z-1)^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$\frac{1}{\lambda_{K_\beta}} = R(Z-1)^2\left[\frac{1}{1^2} - \frac{1}{3^2}\right]$$

$$\frac{1}{\lambda_{K_\gamma}} = R(Z-1)^2\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$

.....



For L-series characteristic X-rays

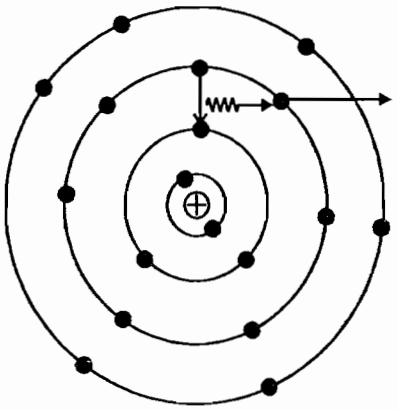
$$\Rightarrow \quad \frac{1}{\lambda_{L_\alpha}} = R(Z-7.4)^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

Similarly, for L_β, L_r, L_δ lines, we can write formule for wavelengths.

CAREER ENDEAVOUR

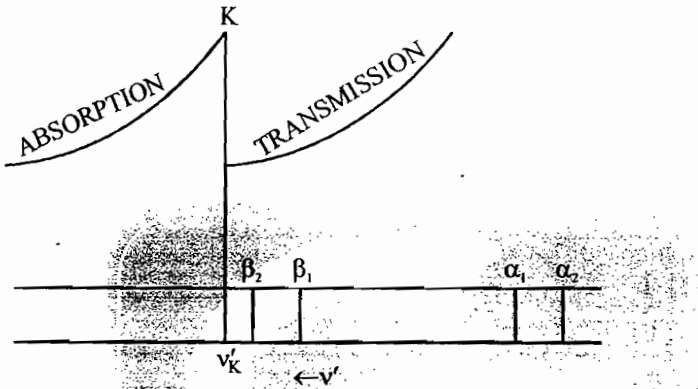
Auger effect or inner photoelectric effect:

Augur founded that the x-ray photon which is created by the transition of an electron in inner shells may be absorbed by any atomic electron and then the electron comes out rather than X-ray photon. Thus the intensity of X-ray photons decreases. This is called Auger effect.



X-ray Absorption Spectra:

When a beam of continuous X-rays is passed through the film of a substance and the transmitted beam is sent into an X-ray spectrograph, an X-ray absorption spectrum of that substance is obtained. The nature of this spectrum is quite different from the X-ray emission spectrum of the same substance. None of the emission lines K_α, K_β ..... appears in the absorption spectrum. Instead, the (absorption) spectrum shows a continuous region of absorption bounded by a sharp edge in the position of the limit of the emission K-series (Figure). When successive elements in the periodic table are used as absorbers, the edge shifts toward higher frequency. Thus, these edges are characteristic of the absorber element and are called 'absorption edges'. In each case, the frequency ν_K' of the absorption edge is called 'K-absorption limit' of the particular element. Frequencies higher than ν_K' are strongly absorbed; lower frequencies are almost transitted.



Example: There are two features of the X-ray absorption spectrum which are to be explained :

(i) Absence of Discrete Absorption Lines : The K_α -line (for example) in emission occurs when an electron drops from the L-shell to the K-shell. In absorption, this line would occur only if an electron from the K-shell, after absorbing an X-ray photon of the required energy from the continuous beam, could go to the L-shell. But this does not happen because the L-shell has already its full quota of 8 electrons and so it cannot receive any further electron (pauli's exclusion principle). Hence the K_α -line cannot be observed as absorption line. This is true for all the X-ray emission lines that are commonly observed.

(ii) Appearance of Sharp Absorption Edges : An X-ray photon can, however, be absorbed by an atom if it has enough energy to remove an inner electron to infinity where the shells no longer exist. If W_K is ithe energy required to remove a K-electron, then a photon of frequency ν' can eject a K-electron provided $\nu' \geq \nu_K'$, where

$$h\nu_K' = W_K .$$

Photons of frequency lower than ν_K' would be transmitted by the absorbing element. At the frequency ν_K', absorption in the K-shell suddenly starts and thereafter continues for all frequencies higher than ν_K'. Hence an absorption continuum is observed.

As Z increases, W_K increases because of the increasing nuclear attraction, and so ν_K' also increases. Hence for successive elements in the periodic table the absorption edge shifts towards higher frequency.

Thus, the K-absorption edge observed in X-ray spectra of elements corresponds to the photoelectric ejection of an electron from the K-shell of that element; its frequency ν_K' gives exactly the required energy W_K. This means that the K-absorption edge directly gives the K energy level. Absorption beyond the edge indicates that the K-electron passes to infinity with kinetic energy E_K given by Einstein's photoelectric equation $\left(E_K = h\nu' - W_K = h\nu' - h\nu_K'\right)$. Since each element gives only one K-absorption edge, we conclude that the K-shell has only a single energy level.

THE BREADTH OF SPECTRAL LINES

Many spectral lines have an observable breadth even when examined under the best optical system. Infact even the sharpest lines have a finite breadth, indicating that the corresponding photons have wavelengths which are not precisely defined but vary over a range of wavelengths. The intensity distribution of a typical spectral line may be expressed by an intensity (I) versus wave number (ν) curve as shown in figure (below).

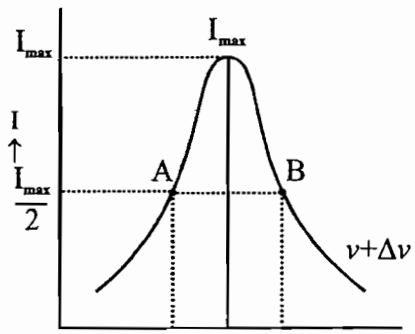


Fig.

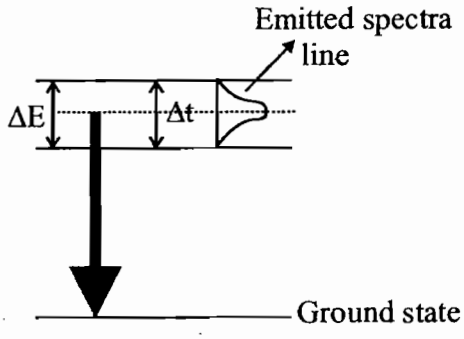
The breadth of a spectral line is defined as the seperation in cm^{-1}, between two points A and B whose intensities are half that of maximum intensity (FWHM). The known causes of spectral-line breadth are the following:
(i) Natural breadth,
(ii) Doppler effect,
(iii) External effects: collision damping, pressure broadening and Stark effect.

Natural Breadth:

The spectral lines arise as a result of electron transitions between two energy levels. According to quantum mechanics, the energy levels of an atom are not discrete, but each has finite energy-breadth, ΔE, in which the probability distribution is concentrated in regions where the terms are observed (figure). A transition between two such levels cannot give an infinitely sharp spectral line. From Heisenberg uncertainty principle, the energy-spread ΔE of a state and the mean time Δt for which the atom remains in that state are related by

$$\Delta E.\Delta t \sim \hbar$$

CAREER ENDEAVOUR



Writing $h\Delta\nu$ for the uncertainty ΔE in energy (because $E = h\nu$, where ν is frequency); and τ (the mean life) for the time Δt, we get

$$(h\,\Delta\nu)\tau \sim h$$

or

$$\Delta\nu \sim \frac{1}{\tau}.$$

It thus follows that greater the mean life of the atom in a particular state, the smaller is the energy-breadth of that state. Hence, the ground states, and the metastable states of atoms are sharp, whereas other states are broad. Thus, the inherent property of the atom that it remains only for a 'finite' time in an excited state gives a natural breadth to the spectral line, independent of all external effects.

Quantum mechanically, the half-intensity breadth of a spectral line due to transition from an excited state to the ground state is given by

$$\Delta\nu = \frac{1}{2\pi\tau}.$$

For an ordinary excited sate, $\tau \approx 10^{-8} s$.

$$\therefore \quad \Delta\nu = \frac{1}{2\pi \times 10^{-8}\,\text{sec}} \approx 10^{7}\ \text{sec}^{-1} \qquad \ldots (1)$$

In terms of wavelength (λ) unit,

$$\nu = \frac{c}{\lambda} \Rightarrow \quad \Delta\nu = -\frac{c}{\lambda^2}\Delta\lambda \qquad \ldots (2)$$

Putting equation (2) in equation (1), we have

$$\frac{c}{\lambda^2}\Delta\lambda = 10^{7} \quad \Rightarrow \quad \Delta\lambda = \frac{\lambda^2}{c} \times 10^{7}$$

For visible light $\lambda \sim 6000\,\text{Å} = 6\times10^{-9}\,m$ & $c = 3\times10^{8}\ m/\text{sec}$

$$\therefore \quad \Delta\lambda \sim 10^{-14}\,m \quad \Rightarrow \quad \Delta\lambda \sim 10^{-4}\,\text{Å}$$, which is very small.

Doppler Effect:

By doppler effect if the emitted atom is in rapid random motion, the actual frequency ν_0 seems to be change to the observer. If the apparent frequency is ν and v is the velocity of the source or atom, then motion of source observer.

$$\nu = \nu_0\left(1 \pm \frac{v}{c}\right)$$

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$$\Rightarrow \quad \nu - \nu_0 = \pm\frac{\nu_0 v}{c} \qquad \ldots (1)$$

Assuming Maxwellian distribution of velocities, the probability that the velocity of an atom of an ideal gas lies between v and $v + dv$ is given by

$$dP = 4\pi\left(\frac{\mu}{2\pi RT}\right)^{3/2} \exp\left[-\frac{\mu v^2}{2RT}\right] v^2 dv \qquad \ldots (2)$$

where μ is the atomic wave R the universal gas constant and T the absolute temperature.

$$\text{or,} \quad I(\nu) = C\exp\left[-\frac{\mu c^2(\nu-\nu_0)^2}{2RT\nu_0^2}\right] \qquad \ldots (2)\ [\text{Using equation (1)}]$$

$$\Rightarrow \quad I|_{\max} = C\,[\text{at } \nu = \nu_0]$$

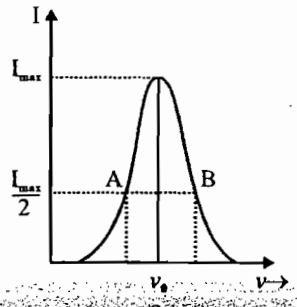
The intensity is half of maximum intensity at point A and B, where

$$\exp\left[-\frac{\mu c^2(\nu-\nu_0)^2}{2RT\nu_0^2}\right] = \frac{1}{2}$$

$$\Rightarrow \quad \nu - \nu_0 = \pm \frac{\nu_0}{c}\sqrt{\frac{2RT}{\mu}\log_e 2}$$

The line breadth $\delta\nu = 2(\nu - \nu_0) = 1.67\frac{\nu_0}{c}\sqrt{\frac{2RT}{\mu}}$ (As $\log_e 2 = 0.693$)

This equation shows that the Doppler broadening is (i) proportional to the square-root of the temprature, (ii) proportional to the frequency ν_0, and (iii) inversely proportional to the square-root of the atomic weight.



Also $\frac{\delta\nu}{\nu_0} = \frac{\delta\lambda}{\lambda_0}$

$$\Rightarrow \quad \boxed{\delta\lambda = 1.67\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}}}$$

where λ is line breadth in terms of wavelength.

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SOLVED PROBLEMS

1. Calculate minimum value of potential that must be applied to produce X-ray photon of $\lambda = 0.1\text{Å}$

Soln. $V_0 = \dfrac{12375}{\lambda_{min}} = \dfrac{123750}{1} = 1.25\times10^5\ V$

2. If the K_α radiation of $Mo(Z=42)$ has a wavelength of 0.71 Å. Calculate the λ corresponding to $Cu(Z=29)$.

Soln. $\dfrac{\lambda_{Cu}}{\lambda_{M_0}} = \dfrac{(Z_{m_0}-1)^2}{(Z_{Cu}-1)^2} = \dfrac{(41)^2}{(28)^2} \quad \Rightarrow \lambda_{Cu} = 1.52\text{Å}$

3. How much energy goes to quantum state emitted when an L-electron (n = 2 state) drops to K-state (n = 1 state) in Cu (Z = 29). Given
R = 109737 cm^{-1}, 1 cm^{-1} = 1.239×10^{-4} eV/cm^{-1}.

Soln. By Moseley's law, X-ray wavelength emitted is given by

$$\frac{1}{\lambda} = R(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{3}{4}R(Z-1)^2 \quad \text{correspond to } K_\alpha \text{ line}(\sigma=1)$$

$$\Rightarrow \frac{1}{\lambda} = \frac{3}{4}(109737\ cm^{-1})(28)^2 = 6.4525\times10^7\ cm^{-1}$$

Corresponding energy emitted is given by $E = 7994.6\ eV$

4. If the series limit of Balmer series for Hydrogen is 346.6 cm. Calculate the atomic number of element which give X-ray wavelength down to 0.1 nm. (i.e. K-series).

Soln. Balmer series for Hydrogen is $\dfrac{1}{\lambda} = R\left(\dfrac{1}{2^2}-\dfrac{1}{n_2^2}\right)$

If series limit $(n_2=\infty)$ is $\lambda_\infty = 346.\lambda\ cm$

$$\frac{1}{\lambda_\infty} = R\left(\frac{1}{2^2}-\frac{1}{\infty}\right) = \frac{R}{4} \quad \Rightarrow R = \frac{4}{\lambda_\infty} = \frac{4}{346.6}\ nm$$

By Moseley's law:

$$\frac{1}{\lambda} = R(z-1)^2\left(\frac{1}{1^2}-\frac{1}{n^2}\right)$$

For minimum λ of this series occur when $n=\infty$,

$$\frac{1}{\lambda} = R(Z-1)^2$$

$$\Rightarrow (Z-1)^2 = \frac{346.6}{4\times0.1\ nm} = 911.5$$

$$\Rightarrow Z-1 = 30.2$$

$$\Rightarrow Z = 31.2 \Rightarrow Z = 31$$

5. If the K, L, M energy levels of platinum involved in the emission of k-series of X-rays of this element are 78,000, 12000, 3000 eV respectively. Calculate the wavelegth λ of K_α and K_β lines.

Soln. K_α line observed when electron drop from L-shell to K-shell:

$$h\nu = \frac{hc}{\lambda_{k_\alpha}} = E_1 - E_2 = 78000 - 12000 = 66000\ eV = 66000\left(1.6\times10^{-19}\right)J$$

For K_α, $\quad \frac{1}{\lambda_{k_\alpha}} = \frac{6600\times\left(1.6\times10^{-19}\right)J}{\left(6.6\times10^{-34}\,J-s\right)\left(3\times10^{8}\ m/s\right)} \quad \Rightarrow \lambda_{k_\alpha} = 0.189\times10^{-10}\,m$

For K_β, $\quad h\nu_{K_\beta} = 78000 - 3000 = 75000\ eV$

6. Calculate the Doppler half-intensity breadth of sodium D-lines at 5893Å corresponding to a temperature of 500 K. R = 8.31 Joule/mole-K, $c = 3\times10^{8}\ m/s$, atomic weight of $Na = 22.99$ gm/mole.

Soln. $\delta\lambda = 1.67\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}}$

$$= 1.67\frac{\left(5893\times10^{-10}\,m\right)}{\left(3\times10^{8}\,m/\sec\right)}\sqrt{\frac{2\times8.31\times500K(\text{Joule/mole }K)}{22.99\times10^{-3}\ Kg/mole}}$$

$\Rightarrow \delta\lambda = 0.02\,\text{Å}$.

7. A spectroscopic examination of the light from a certain star shows that the apparent wavelength of a certain line is 5001Å, whereas the observer wavelength of the same line is produced by a terrestrial source is 5000Å. In what direction and with what speed of the star is moving relative to the earth.

Soln. The apparent wavelength is increased, indicating that the star is moving away from the observer situated on earth.

If λ the apparent wavelength and λ_0 the actual wavelength (when the source is at rest), we have

$$\lambda = \lambda_0\left[1+\frac{v}{c}\right]$$

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or $\quad \frac{\lambda}{\lambda_0} = 1+\frac{v}{c}$.

$\therefore \quad v = c\left(\frac{\lambda}{\lambda_0}-1\right)$

$$= 3.0\times10^{8}\,\text{m/s}\left(\frac{5001\,\text{Å}}{5000\,\text{Å}}-1\right)$$

$$= \frac{3.0\times10^{8}\times1}{5000} = 6.0\times10^{4}\,\text{m/s}$$

8. Group I lists some physical phenomena while Group II gives some physical parameters. Match the phenomena with the corresponding parameter. [GATE-2009]

Group I	Group II
P. Doppler Broadening	1. Moment of inertia
Q. Natural Broadening	2. Refractive index
R. Rotational spectrum	3. Lifetime of the energy level
S. Total internal reflection	4. Pressure

(a) P-4, Q-3, R-1, S-2 (b) P-3, Q-2, R-1, S-4

(c) P-2, Q-3, R-4, S-1 (d) P-1, Q-4, r-2, S-3

Soln. P : Doppler broadening gives pressure.

Q : Natural broadening gives life time of the energy level

R : Rotational spectrum gives moment of inertia

S : Total internal reflection gives refractive index

Hence, correct option is (a).

9. Match the typical spectroscopic regions specified in List-I with the corresponding type of transition in List-II and find the correct answer using the codes given below the list : [GATE-2012]

List-I	List-II
P. Infrared region	1. Electronic transitions involving valence electrons
Q. Ultraviolet visible region	2. Nuclear transitions
R. X-ray region	3. Vibrational transitions of molecules
S. γ - rays region	4. Transitions involving inner shell electrons

Codes :

	P	Q	R	S
(a)	1	3	2	4
(b)	2	4	1	3
(c)	3	1	4	2
(d)	4	1	2	3

Soln. P. Infrared region — 3. Vibrational transitions of molecules

Q. Ultraviolet visible region — 1. Electronic transitions involving valence electrons

R. X-ray region — 4. Transitions involving inner shell electrons

S. γ - rays region — 2. Nuclear transitions

Hence, correct option is (c).

10. A beam of X-ray of intensity I_0 is incident normally on a metal sheet of thickness 2 mm. The intensity of the transmitted beam is $0.025I_0$. The linear absorption coefficient of the metal sheet (in per m) is _____ (upto one decimal place) [GATE-2015]

Soln. The intensity of transmitted beam through the metal sheet of thickness x can be written as

$$I = I_0 \exp(-\mu x) \quad \ldots (i)$$

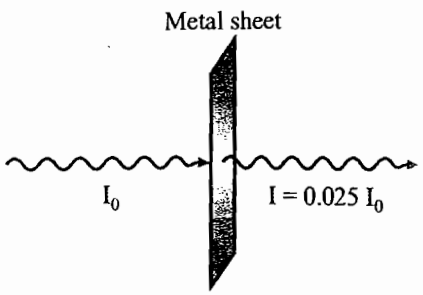
where, μ is the absorption coefficient of the metal sheet

$$\Rightarrow 0.025\, I_0 = I_0 \exp(-\mu \times 2 \times 10^{-3})$$

$$\Rightarrow 0.025 = \exp(-2 \times 10^{-3}\mu)$$

$$\Rightarrow \frac{25}{1000} = \exp(-2 \times 10^{-3}\mu)$$

$$\Rightarrow \mu = \frac{\log 40}{2 \times 10^{-3}} = 1.8446 \times 10^{3}/\text{m}$$



Hence, correct answer is 1.8446×10^3.

11. X-rays are produced using cobalt ($Z = 27$) as target. It was observed that the X-ray spectrum contained a strong K_α line of wavelength 0.1785 nm and a weak K_α line of wavelength 0.1930 nm. Then the weak K_α line is due to an impurity whose atomic number is **[GATE-2001]**

(a) 25 (b) 26 (c) 28 (d) 30

Soln. According to Moseley's law :

$$\bar{\nu} \propto (Z - \sigma)^2 \quad \ldots (i)$$

Here, for strong K_α line

$$\frac{1}{0.1785 \text{ nm}} \propto (27 - 1)^2 \quad \ldots (ii)$$

and for weak K_α line

$$\frac{1}{0.1930 \text{ nm}} \propto (Z - 1)^2 \quad \ldots (iii)$$

Here, we have used $\sigma = 1$ as screening factor.

Now, from equations (ii) and (iii), we have

$$\frac{\left(\frac{1}{0.1785 \text{ nm}}\right)}{\left(\frac{1}{0.1930 \text{ nm}}\right)} = \frac{(26)^2}{(Z-1)^2}$$

$$\Rightarrow \quad (Z-1)^2 = \frac{0.1785 \times 26^2}{0.1930} = 625 \quad \Rightarrow \quad z - 1 = 25 \Rightarrow 26$$

Hence, correct option is (b).

12. The L_β line of X-rays emitted from an atom with principal quantum numbers $n = 1, 2, 3, \ldots$ arises from the transitions **[GATE-2005]**

(a) $n = 4 \rightarrow n = 2$ (b) $n = 3 \rightarrow n = 2$ (c) $n = 5 \rightarrow n = 2$ (d) $n = 3 \rightarrow n = 1$

Soln. For Lyman series : $\bar{\nu} = \frac{1}{\lambda} = R_\infty \left(\frac{1}{1^2} - \frac{1}{n^2}\right)$, where $n = 2, 3, 4, 5, \ldots$

For L_β, the transition will be from $n = 3$ to $n = 1$.

Hence, correct option is (d).

13. The target of an X-ray tube is subjected to an excitation voltage V. The wavelength of the emitted X-rays is proportional to **[GATE-2006]**

(a) $\frac{1}{\sqrt{V}}$ (b) $\sqrt{V}$ (c) $\frac{1}{V}$ (d) V

Soln. The wavelength of the emitted X-rays is proportional to excitation voltage V.

i.e., $\lambda = \frac{hc}{eV} \Rightarrow \lambda \propto \frac{1}{V}$.

Hence, correct option is (c).

14. The short wavelength cut-off of the continuous X-ray spectrum from a nickel target is 0.0825 nm. The voltage required to be applied to an X-ray tube is **[GATE - 2003]**

(a) 0.15 kV (b) 1.5 kV (c) 15 kV (d) 150 kV

Soln. For X-ray, $\lambda = \frac{hc}{eV} \Rightarrow V = \frac{hc}{e\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{1.6\times10^{-19}\times0.0825\times10^{-9}} = 150\times10^{2}\,V = 15\times10^{3}\,V = 15\,kV.$

Hence, correct option is (c).

15. A continuous monochromatic ($\lambda = 600$ nm) laser beam is chopped into 0.1 ns pulses using salt of shutter. Find the resultant linewidth $\Delta\lambda$ of the beam in units of 10^{-3} nm. **[TIFR - 2016]**

Soln. Wavelength (λ) = 600 nm = 600 × 10^{-9} m.
Time (t) = 0.1 ns = 0.1 × 10^{-9} sec.

The line width $\Delta\lambda = \frac{\lambda^2}{c}\Delta\nu = \frac{\lambda^2}{c}\cdot\frac{1}{t}$ $\left(\because \Delta\nu = \frac{1}{t}\right)$

$$= \frac{(600\times10^{-9})^2}{(3\times10^{8})}\times\frac{1}{(0.1\times10^{-9})} = \frac{36\times10^{4}\times10^{-18}}{3\times10^{8}\times1\times10^{-10}} = 12\times10^{-12}\,m = 12\times10^{-3}\,nm.$$

Hence, correct answer is (12).

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Chapter 6

Pure Rotational Spectra

Diatomic Molecule : A stable arrangement of two atoms (nuclei and electrons), separated by a distance is called as diatomic molecule.

Homonuclear and Heteronuclear Molecule : A molecule is said to be homonuclear if the atoms forming the molecule are similar. The examples of homonuclear molecules are H_2, N_2, O_2,.... molecules.

On the other hand, if the atoms forming the molecule are different, then molecule is called as heteronuclear molecules. The examples of this type of molecules are HCl, CN, CO_2,.... molecules.

Internuclear axis : In a diatomic molecule, the line joining the constituent atoms, is called as internuclear axis.

Molecular spectra : When light from a source containing a source in molecular state is sent into a spectrometer, more or less broad wavelength regions are observed in the spectrum. These regions are called bands, and the spectrum is called as band spectrum or molecular spectra.

Types of molecular spectra:

The molecular spectra can be divided into three spectral ranges corresponding to the different types of transitions between molecular energy levels.

(i) **Electronic spectra :** This type of spectra is observed both in emission and absorption in the visible and ultraviolet regions. The electronic spectra are observed for the heteronuclear as well as for homonuclear diatomic molecules, i.e., HCl, HBr, H_2, N_2, O_2 etc. In these spectra, each spectrum consists of quite a large number of bands. Each band has a sharp edge which is called as band head where the intensity falls abruptly to zero value, and from this edge the intensity falls off gradually to the other side of the band. Under high resolution, a band is found to be composed of a series of lines which exist farther apart from the band head. The band is called as "degraded" toward the side opposite to the band-head.

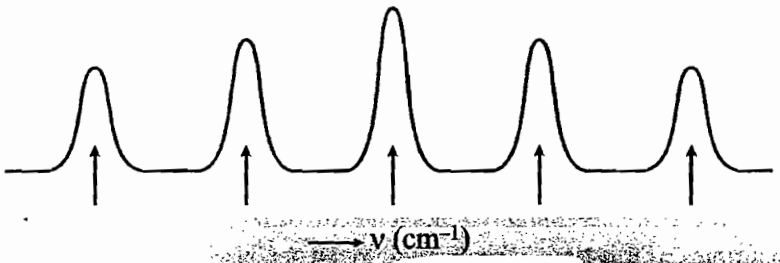
(ii) **Vibrational-rotational spectra :** This type of spectra is observed in absorption, in the near infrared region ($1\mu - 10^2\mu$; $1\mu = 10^{-6}$ m $= 10^4$ Å). Each spectrum consists of an intense band, called fundametal band which is accompanied by a few weak bands. These bands, like electronic bands, have a fine structure. These spectra are observed only for heteronuclear diatomic molecules. These spectra are not produced by molecules like H_2, O_2, N_2, etc.

(iii) **Pure rotational spectra :** This type of spectra is observed in absorption in the far infrared ($10^2\mu - 10^3\mu$) or in the microwave ($10^3\mu - 10^4\mu$) region. Each spectrum is composed of a series of nearly equidistant lines. Like vibrational-rotational spectra, the pure rotational spectra are observed only for the heteronuclear diatomic molecules i.e., this type of spectra arise in only those molecules which have permanent dipole moment.

PURE ROTATIONAL SPECTRA

Sailent features of pure rotational spectra : Pure rotational spectra arise from transitions between rotational energy levels, and are observed in the far infrared ($\approx 10^2\mu - 10^3\mu$) or microwave ($\approx 10^3\mu - 10^4\mu$) region of the electromagnetic spectrum. Only molecules that have permanent electric dipole moments can absorbs or emit electromagnetic radiation in such transitions. This means that homonuclear diatomic molecules such as H_2, O_2, N_2 ; symmetric linear molecules such as CO_2 (O = C = O), and spherical top polyatomic molecules such as CH_4 do not exhibit rotational spectra.

In practice, this spectra are observed in absorption. For heteronuclear diatomic molecules such as HF, HCl, HBr, CO etc. the rotational spectra consists of a simple series of absorption maxima which are very nearly equidistant on a wave number scale (see figure below).

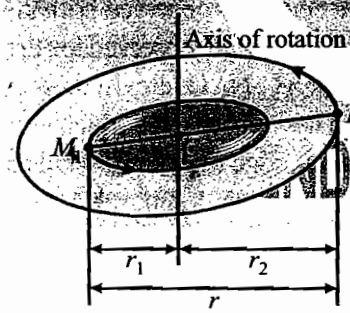


A measurement of frequencies of these maxima leads to determination of the moment of inertia and internuclear distance of the molecule.

For homonuclear molecules, which do not give the rotational spectra, the moment of inertia and the internuclear distance can be found from the rotational fine structure of electronic bands and from rotational Raman spectra.

Explanation of pure rotational rotator :

The molecule as a rigid rotator : The simplest example of this rotating diatomic molecule is that of a rigid rotator, that is the internuclear separation is assumed to be fixed at the equilibrium value.



Let us consider two atoms of masses M_1 and M_2 which are chemically bonded to from a diatomic molecule (see figure above). The atom may be treated as point masses because their masses are concentrated in their nuclei which have a size of the order of 10^{-15} m, much smaller than the order of internuclear separation ($\approx 10^{-10}$ m).

Let r be the distance between M_1 and M_2 and r_1 and r_2 are the respective distances of the atoms from the molecular center of mass C.

This system is capable of rotation about an axis passing through its center of mass C and perpendicular to the internuclear axis.

From the definition of center of mass,

$$M_1 r_1 = M_2 r_2 \qquad \ldots (i)$$

also, $$r = r_1 + r_2 \qquad \ldots (ii)$$

From these equations, we can write,

$$r_1 = \frac{M_2}{(M_1 + M_2)} r \text{ and } r_2 = \frac{M_1}{(M_1 + M_2)} r \quad \text{... (iii)}$$

Now, the moment of inertia of this system about the axis of rotation, perpendicular to internuclear axis and passing through the centre of the mass is given by

$$I = M_1 r_1^2 + M_2 r_2^2$$

Putting values of r_1 and r_2 from equation (iii), we get

$$= M_1 \left[\frac{M_2}{M_1 + M_2}\right]^2 r^2 + M_2 \left[\frac{M_1}{M_1 + M_2}\right]^2 r^2 = \frac{M_1 M_2}{(M_1 + M_2)} r^2$$

$$\Rightarrow I = \mu r^2 \quad \text{... (iv)}$$

where, $\mu = \frac{M_1 M_2}{M_1 + M_2}$ is the "reduced mass μ" of the molecule.

Thus, the diatomic molecule is equivalent to a single point mass μ as a fixed distance r from the axis of rotation such a system is called as rigid rotator.

In order to determine the possible energies of rotation of the molecule, we have to solve the Schrödinger equation of a rigid rotator, which is

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} E\psi = 0 \quad \text{... (v)}$$

The potential energy term V is zero because r is fixed. In spherical polar coordinates, the equation can be written as

$$\frac{1}{r^2 \sin^2\theta} \frac{\partial}{\partial \theta}\left[\sin\theta \frac{\partial \psi}{\partial \theta}\right] + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} E\psi = 0 \quad \text{... (vi)}$$

Solving above equation, we get

$$E = \frac{I^2}{2I}$$

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$$\Rightarrow \quad E \text{ or } E_j = \frac{J(J+1)\hbar^2}{2I} \quad \text{... (vii)}$$

where, J is the rotational quantum number which can take only positive integral values i.e., $J = 0, 1, 2, 3, ...$

Thus, we can say that rigid rotator have a discrete set of energy levels. From classical mechanics,

$$\left.\begin{aligned} E &= \frac{1}{2} I \omega^2 \\ \text{and} \quad L &= I\omega \end{aligned}\right\} \quad \text{... (viii)}$$

so that $L = \sqrt{2EI}$

Thus, the angular momentum L of the system in the quantum state J is given by

$$L = \sqrt{\frac{2Ih^2 J(J+1)}{8\pi^2 I}}$$

$$\Rightarrow \quad L' = \frac{h}{2\pi}\sqrt{J(J+1)} \quad \text{... (ix)}$$

Now, rotational angular frequency

$$\omega = \frac{L}{I} = \frac{h}{2\pi I}\sqrt{J(J+1)} \qquad \ldots (x)$$

$\therefore \quad \omega = 2\pi\nu_{rot}$

$\Rightarrow \quad \nu_{rot}$ = rotational frequency $= \dfrac{\omega}{2\pi}$

$$= \frac{h}{2\pi^2(2I)}\sqrt{J(J+1)}$$

$\Rightarrow$

$$\nu_{rot} = \frac{h}{4\pi^2 I}\sqrt{J(J+1)} \qquad \ldots (xi)$$

Rotational spectra : Now, let us investigate the spectrum expected from a rigid rotator. In terms of wave number, the energy equation can be given as (from equation (vii)).

$$F(J) = \frac{E}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1}$$

$$F(J) = BJ(J+1) \qquad \ldots (xii)$$

where, $B = \dfrac{h}{8\pi^2 Ic}$, is known as rotational constant.

Substituting $J = 0, 1, 2, \ldots$ we get

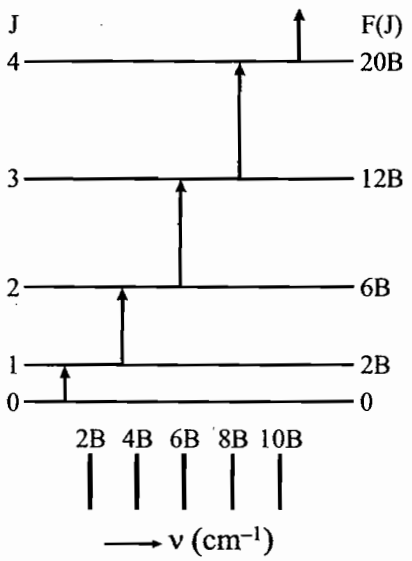
$F(J) = 0, 2B, 6B, 12B, 20B, \ldots$

Thus, we have a series of discrete rotational energy levels (whose spacings increase with increasing J (see figure below). The wave number of the emitted or absorbed radiation would be given by

$$\nu = F(J') - F(J'')$$

$$= BJ'(J'+1) - BJ''(J''+1) \qquad \ldots (xiii)$$

A study of the matrix element of the dipole moment shows that the rotational transitions can only occur such that J changes by unity, so that the selection rule is



$\Delta J = \pm 1$

since, we have chosen $J' > J''$, we have $J' = J'' + 1$

Thus,

$$\nu = B(J''+1)(J''+2) - BJ''(J''+1)$$

$$= B(J''^2 + 3J'' + 2 - J''^2 - J'')$$

$$\Rightarrow \quad \nu = 2B(J''+1) \qquad \ldots (xiv)$$

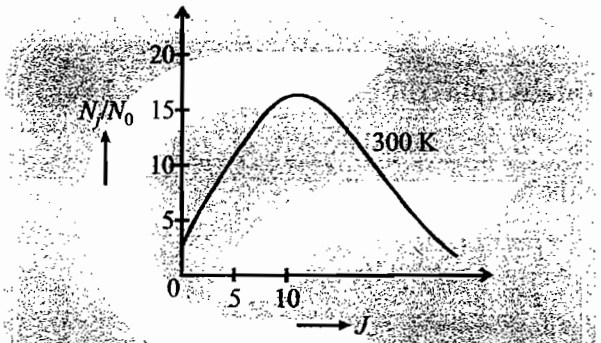
Substituting $J = 0, 1, 2, \ldots$ we get

$$\nu = 2B, 4B, 6B, 8B, \ldots.$$

Thus, the absorption spectrum of a rigid rotator is expected to consists of a series of equidistant lines with constant separation $2B$, provided transitions start from various energy levels $J = 0, 1, 2, 3, \ldots.$ as shown. This however, does take place because quite a good number of rotational energy levels are well populated even at ordinary temperatures.

The population in the J^{th} level relative to the lowest level, in thermal equilibrium at a temperature K kelvin is

$$\frac{N_j}{N_0} = (2J+1)e^{-(E_j - E_0)/k_B T} = (2J+1)e^{-BJ(J+1)hc/k_B T}$$



A graph between N_j/N_0 and J for a typical molecule (300 K) is shown in the figure.

Experimentally, the far infrared spectrum of HF, for example shows a series of approximately equidistant absorption maxima, and the mean spacing is found to be 40.5 cm^{-1}. From above, we have $2B = 40.5\ cm^{-1}$ where

$$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2(\mu r^2)c}$$

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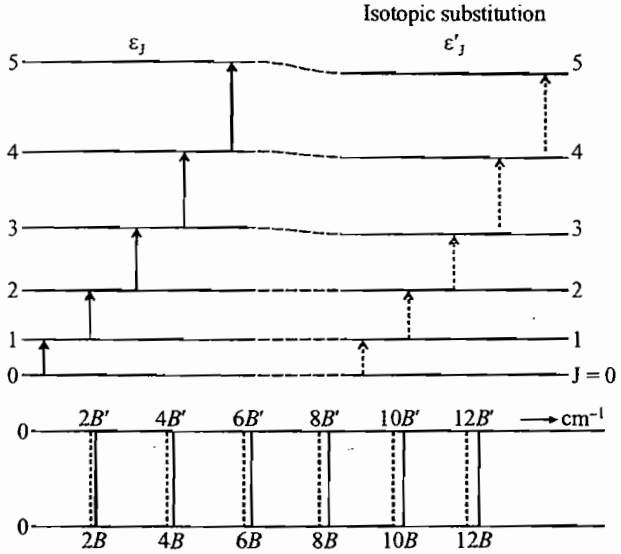
From this, the value of $r = 0.937$ Å which fairly agrees with the values obtained from gas viscosity and crystal structure measurement. Hence, we can say that the far-infrared spectrum is a rotational spectrum.

Effect of Isotopic Substitution:

When a particular atom in a molecule is replaced by its isotope an element identical in every way except for its atomic mass the resulting substance is identical chemically with the original. In particular there is no appreciable, change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in moment of inertia and B values for the molecule.

If B' be the rotational constant for the heavier isotope then $B' < B$ and so on $\varepsilon'_J < \varepsilon_J$. Thus, the separation of levels for the heavier isotope will be smaller than those of the corresponding levels of the lighter isotope. Hence spectral lines will also be closer [as shown in figure].



[The effect of isotope substitution on the energy levels and rotation spectrum of a diatomic molecule].

Observation of the decreased sparation between the lines ($2B'$) has led to the evaluation of precise atomic weights.

Example : First rotational absorption of $^{12}C\,O^{16}$ to be found at 3.84235 cm^{-1}, while that of $^{13}C\,^{16}O$ was at 3.67337 cm^{-1}. The values of B determined from these figures are : $B = 1.92118$ cm^{-1}, $B' = 1.83669$ cm^{-1}, where the prime refers to the heavier molecule.

$$\text{So, } \frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is the reduced mass, and the internuclear distance is considered unchanged isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00,

$$\text{we have : } \frac{\mu'}{\mu} = 1.046 = \frac{15.9994\,m'}{15.9994 + m'} \times \frac{(12 + 15.9994)}{12 \times 15.9994}$$

So, $m' = 13.0007$. Thus, mass of ^{13}C is 13.0007.

Note: The data obtained above were obtained from $^{13}C\,^{16}O$ molecules in natural abundance (i.e. about 1 per cent of ordinary carbon monoxide). Thus besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

The non-rigid rotator :

If the separation between successive lines was calculated for a large number of J's, it was formed that the separation between successive lines ($2B$) decreases steadily with increasing J.

In fact the reason for this decarese may be the increase in internuclear distances with increasing J. The bond length increases with J and we can see that our assumption of a rigid bond is only an approximation, in fact, of course, all bonds are elastic to some extent, and the increase in length with J merely reflects the fact that the more a diatomic molecule rotates the greater is the centrifugal forces tending to move the atoms apart.

This elasticity will have two consequences :

1. When the bond is elastic, a molecule may have vibrational energy - i.e. the bond will stretch and compress periodically with a certain fundamental frequency dependent upon the masses of the atoms and the elasticity of the bond. The force constant is given by, $k = 4\pi^2 \bar{\omega}^2 c^2 \mu$, $\bar{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$. Plainly, the variation of B with J is determined by the force distort under centrifugal forces.

2. The second consequence of elasticity is that the quantities r and B vary during a vibration. But in rotational spectra, variation in r and B will be too small to be ignored.
The schrödinger equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be :

$$\boxed{E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ Joule}}$$

or,

$$\boxed{\varepsilon_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}} \quad \text{... (i)}$$

where, the rotational constant, $B = \frac{h}{8\pi^2 IC}$ cm^{-1} and the centrifugal distortion constant, $D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$ cm^{-1}.

It is a positive quantity and equation (i) applies for a simple harmonic force field only.

D can be represented in terms of B and $\bar{\omega}$, $D = \frac{4B^3}{\bar{\omega}^2}$

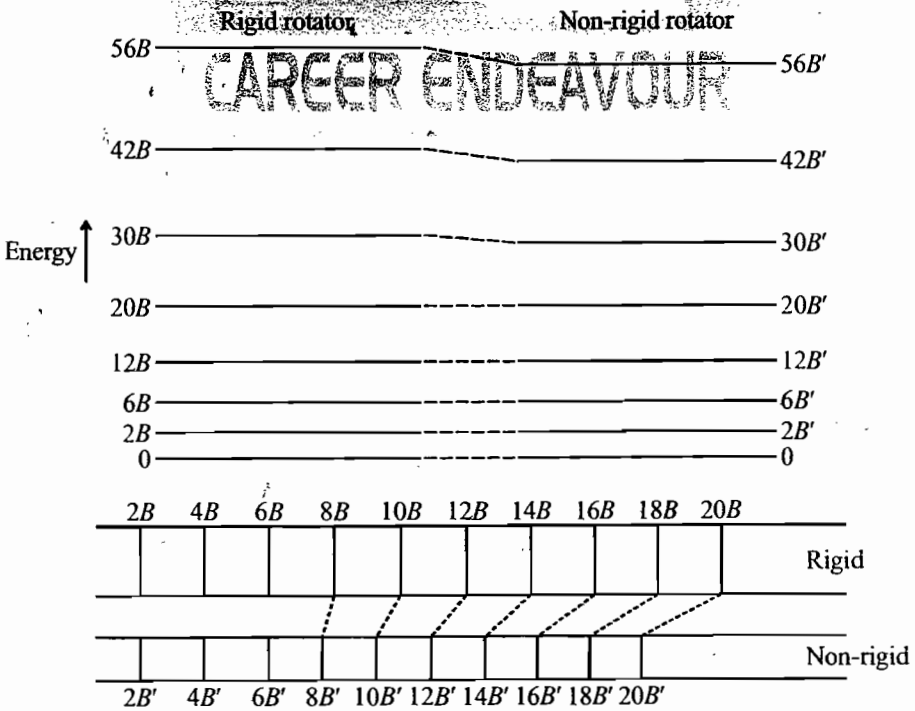
$\bar{\omega}$ is in cm^{-1} and B is in cm^{-1}.
The order of B is found to be 10 cm^{-1} while the order of D being 10^{-3} cm^{-1}.

Rotational spectra : The selection rule for non-rigid rotator is still $\Delta J = \pm 1$.

So, $\varepsilon_{J+1} - \varepsilon_J = B\left[(J+1)(J+2) - J(-J+1)\right] - D\left[(J+1)^2(J+2)^2 - J^2(J+1)^2\right]$

$$\bar{\nu}_J = \boxed{\varepsilon_{J+1} - \varepsilon_J = 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1}}$$

$\bar{\nu}_J$ represents equally the upward transition from J to $J+1$ or the downward from $J+1$ to J. The spectrum of the elastic (non-rigid) rotor is similar to that of the rigid molecule except that each line is displaced slightly to low frequency, the displacement increasing with $(J+1)^3$.



Due to centrifugal term, the increase in spacing between successive rotational levels with increasing J becomes slightly less rapid.

A knowledge of *D* gives rise to two useful informations:

1. Firstly, it allows us to determine the *J* value of lines in an observed spectrum. If three consecutive lines have been measured then the unique values for *B*, *D* and *J* can be obtained using the equation

$$\bar{\nu}_J = 2B(J+1) - 4D(J+1)^3$$

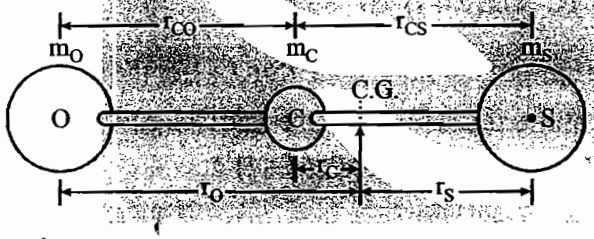
2. A knowledge of *D* enables us to determine although rather in accurately the vibrational frequency of a diatomic molecule $\bar{\omega}^2 = \frac{4B^3}{D}$.

The force constant then follows directly, $k = 4\pi^2 c^2 \bar{\omega}^2 \mu$, $\bar{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$.

Polyatomic molecules :

1. **Linear molecules :** The whole of the discussion on diatomic molecules applies equally to all linear molecules; three points, however should be underlined:
   (a) Since the moment of inertia for the end-over-end rotation of a polyatomic linear molecule is considerably greater than that of a diatomic molecule, the *B* value will be much smaller and $B \approx 1\ \text{cm}^{-1}$ or less.
   (b) OCS will be microwave active, while OCO will not. Infact $^{16}O\,C\,O^{18}$ will also be microwave inactive.
   (c) A non cyclic polyatomic molecule containing *N* atoms has all together $N-1$ individual bond lengths to be determined.

Let us consider the rotation of OCS in detail, where r_O, r_C and r_S represent the distances of the atoms from the center of gravity.



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Consideration of moments gives

$$m_O r_O + m_C r_C = m_S r_S \qquad \ldots (i)$$

The moment of inertia is

$$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2 \qquad \ldots (ii)$$

also, we have

$$r_O = r_{CO} + r_C \text{ and } r_S = r_{CS} - r_C \qquad \ldots (iii)$$

where, r_{CO} and r_{CS} are the bond lengths of the molecule.

Using equation (iii) in equation (i), we get

$$(m_O + m_C + m_S) r_C = m_S r_{CS} - m_O r_{CO}$$

$$\Rightarrow \quad M r_C = m_S r_{CS} - m_O r_{CO} \qquad \ldots (iv)$$

(Let $m_O + m_C + m_S = M$)

Put equation (iii) in equation (ii), we get

$$I = m_O (r_{CO} + r_C)^2 + m_C r_C^2 + m_S (r_{CS} - r_C)^2$$

$$= m_O r_{CO}^2 + m_S r_{CS}^2 + m_O r_C^2 + m_C r_C^2 + m_S r_C^2 - 2r_C (m_S r_{CS} - m_O r_{CO})$$

Using r_C in the above from equation (iv), we get

$$I = m_O r_{CO}^2 + m_S r_{CS}^2 + \frac{M(m_S r_{CS} - m_O r_{CO})^2}{M^2} - \frac{2(m_S r_{CS} - m_O r_{CO})^2}{M}$$

$$\Rightarrow \quad I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})}{M} \qquad \ldots (v)$$

For an isotopic molecule ^{18}OCS, we write m'_O for m_O

$$I' = m'_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m'_O r_{CO} - m_S r_{CS})^2}{M'} \qquad \ldots (vi)$$

Here we assumed that bond lengths do not change with isotopic substitution.

So, we can solve for r_{CO} and r_{CS}, provided we have extracted a value for I' from the microwave spectrum of the isotopic molecule.

2. **Symmetric top molecules :** Consider a rigid symmetric top (for example; NH_3 or CH_3Cl). The Schrödinger equation may be solved to give the allowed energy levels for rotation as $I_B = I_C \neq I_A$ and $I_A \neq 0$

$$\varepsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2 \text{ cm}^{-1}$$

where, $B = \frac{h}{8\pi^2 I_B c}$ and $A = \frac{h}{8\pi^2 I_A c}$

Since energy depends on K^2, so that it is immaterial whether the top spins clockwise or anticlockwise; the energy is the same for a given angular momentum. For all $K > 0$, therefore, the rotational energy levels are doubly degenerate.

The selection rule for this molecule will be $\Delta J = \pm 1$ and $\Delta K = 0$

$\therefore \quad \varepsilon_{J+1,K} - \varepsilon_{J,K} = 2B(J+1)$

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Thus, the spectrum is independent of K, and hence rotational changes about the symmetry axis do not give rise to a rotational spectrum.

The spectrum would be just the same as for a linear molecule and that only one moment of inertia that for end-over-end rotation can be measured.

Chemical analysis by microwave spectroscopy:

The microwave spectrum of a substance is very rich in lines since many rotational levels are populated at room temperatures, but since the lines are very sharp and their position can be measured with great accuracy, observation of just a few of them is sufficient, to establish the presence of a previously examined substance in the sample.

- The technique can not detect the presence of particular molecular groupings in a sample, like – OH or – CH_3.
- It can readily distinguish the presence of isotopes in a sample.
- It can even detect different conformational isomers, provided they have different moments of inertia.
- One important area, where microwave analysis is being used is in the chemical exmination of interstellar space.

SOLVED PROBLEMS

1. The moment of inertia of the CO molecule is $1.46\times10^{-46}\ kg-m^2$. Calculate the energy (in eV) and the angular velocity in the lowest rotational energy level of the CO molecule.

Soln. The quantum-mechanical energy of a rotating diatomic molecule is given by

$$E_J=\frac{h^2}{8\pi^2 I}J(J+1)$$

where, I is the moment of inertia of the molecule about the axis of rotation. The lowest rotational energy level corresponds to J = 1, and for this level in CO

$$E_{J=1}=\frac{h^2\times2}{8\pi^2 I}=\frac{h^2}{4\pi^2 I}$$

Substituting the value of h in M.K.S. units and the given value of I, we have

$$E_{J=1}=\frac{\left(6.62\times10^{-34}\,J-\text{sec}\right)^2}{4\times(3.14)^2\times\left(1.46\times10^{-46}\,kg\,m^2\right)}$$

$$=\frac{6.62\times10^{-34}\times6.62\times10^{-34}}{4\times3.14\times3.14\times1.46\times10^{-46}}$$

$$=7.61\times10^{-23}\,J$$

But 1 eV = $1.6\times10^{-19}\,J$

$$\therefore\quad E_{J=1}=\frac{7.61\times10^{-23}}{1.6\times10^{-19}}$$

$$=4.75\times10^{-4}\,eV$$

The angular velocity of the CO molecule (when J = 1) is

$$\omega=\sqrt{\frac{2E}{I}}\qquad\left(\because E=\frac{1}{2}I\omega^2\right)$$

$$=\sqrt{\frac{2\times7.61\times10^{-23}}{1.46\times10^{-46}}}$$

$$=10.2\times10^{11}\ \text{rad/sec}$$

2. The $J=0\rightarrow J=1$ absorption line in CO occurs at a frequency of 1.153×10^{11} cycles/sec. Calculate the moment of inertia and internuclear separation of CO.

$\left(h=6.62\times10^{-27}\ erg-\text{sec},\ N_A=6.023\times10^{23}\right)$

Soln. The rotational energy of a diatomic molecule is given by

$$E=\frac{h^2}{8\pi^2 I}J(J+1)$$

The energy separation between J = 0 and J = 1 levels is:

$$\Delta E=E_{J=1}-E_{J=0}=\frac{h^2}{4\pi^2 I}$$

The frequency $\bar{\nu}$ absorbed in transition J = 0 → J = 1 is:

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$$\nu' = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}$$

$$\Rightarrow \quad I = \frac{h}{4\pi^2 \nu'} = \frac{6.62\times10^{-27}\ erg-\sec}{4\times(3.14)^2\times\left(1.153\times10^{11}\sec^{-1}\right)}$$

$$= 1.46\times10^{-39}\ gm-cm^2$$

The reduced mass of the CO molecule is given by

$$\mu_{CO} = \frac{M_C M_O}{M_C + M_O}$$

$$= \frac{(12\times16)/\left(6.023\times10^{23}\right)^2}{(12+16)/\left(6.023\times10^{23}\right)}$$

$$= \frac{12\times16}{28\times\left(6.023\times10^{23}\right)} = 1.14\times10^{-23}\,g$$

Therefore, the internuclear separation (bond length) r is

$$r = \sqrt{\frac{I}{\mu}} \qquad \left(\because\ I = \mu r^2\right)$$

$$= \sqrt{\frac{1.46\times10^{-39}\ gm-cm^2}{1.14\times10^{-23}\ gm}}$$

$$= 1.13\times10^{-8}\ cm = 1.13\,\text{Å}$$

3. The OH – radical has a moment of inertia of $1.48\times10^{-40}\ gm-cm^2$. Calculate its internuclear distance. Also calculate, for J = 5, its angular momentum and angular velocity. Determine the energy absorbed in the J = 6 → J = 5 transition in cm^{-1} and erg/molecule.

Soln. The reduced mass of the OH-radical is given by

$$\mu_{OH} = \frac{M_O M_H}{M_O + M_H}$$

$$= \frac{(1\times16)\left(6.023\times10^{23}\right)^2}{(1+16)\left(6.023\times10^{23}\right)^2} = \frac{16}{17\times\left(6.023\times10^{23}\right)} = 1.56\times10^{-24}\ gm$$

If I is the moment of inertia, then the internuclear distanec r is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48\times10^{-40}\ gm-cm^2}{1.56\times10^{-24}\,gm}}$$

$$= 0.97\times10^{-8}\ cm = 0.97\,\text{Å}$$

The angular momentum is given by

$$L = \sqrt{J(J+1)}\,\frac{h}{2\pi}$$

For J = 5, we have

$$L = \sqrt{30} \times \frac{6.62 \times 10^{-27}}{2 \times 3.14} \, erg - \sec = 5.77 \times 10^{-27} \, erg - \sec$$

The corresponding angular velocity is:

$$\omega = \frac{L}{I}$$

$$= \frac{5.77 \times 10^{-27} \, erg - \sec}{1.48 \times 10^{-40} \, gm - cm^2} = 3.90 \times 10^{13} \sec^{-1}$$

The wave number of the radiation absorbed (absorbed energy in cm^{-1}) in transition from J to J+1 is given by

$$v = 2B(J+1)$$

where, J refers to the lower state. Therefore, for the transition $J = 6 \rightarrow J = 5$, we have

$$v = 2B(5+1) = 12B$$

But $B = \frac{h}{8\pi^2 Ic}$ $\quad \therefore \quad v = \frac{12h}{8\pi^2 Ic}$

$$= \frac{12 \times \left(6.62 \times 10^{27} \, erg - \sec\right)}{8 \times (3.14)^2 \times \left(1.48 \times 10^{-40} \, gm - cm^2\right)\left(\times 10^{10} \, cm - \sec^{-1}\right)}$$

$$= 227 \, cm^{-1}$$

The corresponding energy E in erg/molecule is obtained by

$$E = vhc$$

$$= \left(227 \, cm^{-1}\right)\left(6.62 \times 10^{-27} \, erg - \sec\right)\left(3 \times 10^{10} \, cm - \sec^{-1}\right)$$

$$= 4.50 \times 10^{-14} \, erg \, / \, \text{molecule}$$

4. The $J = 1 \leftarrow 0$ transition in HCl occurs at 20.68 cm^{-1}. Regarding the molecule to be rigid rotator, calculate the wavelength of the transition $J = 15 \leftarrow 14$.

Soln. The wave number of the radiation absorbed in a rotational transition from J to J+1 is given by

$v = 2B(J+1)$, where, J refers to the lower state.

For a transition from J = 0 to J = 1, we have

$$v = 2B$$

But $v = 20.68 \, cm^{-1}$ (given)

$\therefore \quad 2B = 20.68 \, \text{cm}^{-1}$

or, $\quad B = 10.34 \, cm^{-1}$

Again, the wave number of the radiation absorbed in $J = 15 \leftarrow 14$ is given by

$v = 2B(J+1)$, where, J refers to lower state.

$$= 2B(14+1) = 2 \times 10.34 \times 15 = 310.2 \, cm^{-1}$$

The corresponding wavelength is

$$\lambda = \frac{1}{v} = \frac{1}{310.2} \, cm$$

$$= 32 \times 10^{-4} \, cm = 32\mu$$

5. The transition J = 3 to J = 4 in HCl molecule is associated with radiation of 83.03 cm^{-1}. Use the rigid-rotator approximation to calculate the moment of inertia and internuclear distance (bond length) of HCl.

Soln. The wave number of absorbed radiation in rotational transition $J \to (J+1)$ is given by

$$v = 2B(J+1)\, cm^{-1}$$, where, J refers to the lower state.

For $J = 3 \to J = 4$, we have

$$v = 2B(3+1) = 8B$$

But $v = 83.03\, cm^{-1}$ (given)

$\therefore$ $8B = 83.03\, cm^{-1}$

$$B = 10.38\, cm^{-1}$$

The rotational constant B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

Therefore, the moment of inertia of the molecule is

$$I = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6.62\times10^{-27}\ erg-\sec}{8\times(3.14)^2\times(10.38\ cm^{-1})(3\times10^{10}\ cm-\sec^{-1})}$$

$$= 2.7\times10^{-40}\ gm-cm^2$$

The reduced mass of HCl molecule is

$$\mu_{HCl} = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

$$= \frac{(1\times35)(6.023\times10^{23})^2}{(1+35)(6.023\times10^{23})}$$

$$= 1.61\times10^{-24}\ gm$$

The internuclear distance (bond length) is therefore

$$r = \sqrt{\frac{I}{\mu}}$$

$$= \sqrt{\frac{2.7\times10^{-40}\ gm-cm^2}{1.61\times10^{-24}\ gm}}$$

$$= 129\times10^{-8}\ cm = 1.29\,\mathring{A}$$

6. The far infra-red spectrum of H^1Br^{79} cosists of a series of lines spaced 17 cm^{-1} apart. Find the internuclear distance of H^1Br^{79} $\left(h = 6.62\times10^{-27}\ erg-\sec\right)$ $\left(= 3.0\times10^{10}\ cm/\sec\right)$, $N_A = 6.023\times10^{23}$

Soln. The wave numbers of the lines in a pure rotational spectrum are given by

$$v = 2B(J+1)$$

where, J refers to the lower rotational quantum numbers. The separation between two successive lines corresponding to J and J+1 is

$$\Delta v = 2B(J+2) - 2B(J+1) = 2B$$

Here, $\Delta v = 17\ cm^{-1}$

$\because$ $2B = 17\ cm^{-1}$

$\Rightarrow$ $B = 8.5\ cm^{-1}$

The moment of inertia of the molecule is

$$I = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6.62\times10^{-27}\ erg-\sec}{8\times(3.14)^2\times(8.5\ cm^{-1})\times(3\times10^{10}\ cm/\sec)}$$

$$= 3.29\times10^{-40}\ gm-cm^2$$

The reduced mass of H^1Br^{79} is

$$\mu_{HBr} = \frac{(1\times79)/(6.023\times10^{23})^2}{(1+79)/(6.023\times10^{23})} = 1.64\times10^{-24}\ gm$$

Therefore, the internuclear distance is

$$r = \sqrt{\frac{I}{\mu}}$$

$$= \sqrt{\frac{3.29\times10^{-40}\ gm-cm^2}{1.64\times10^{-24}\ gm}} = 1.42\times10^{-8}\ cm = 1.42\ \text{Å}$$

7. Consider the pure rotational spectrum of a diatomic rigid rotor. The separation between two consecutive lines $\Delta\bar{\nu}$ in the spectrum **[GATE-2004]**

(a) is directly proportional to the moment of inertia of the rotor
(b) is inversely proportional to the moment of inertia of the rotor
(c) depends on the angular momentum
(d) is directly proportional to the square of the interatomic separation

Soln. For pure rotational spectrum of a diatomic rigid rotor, the separation between two consecutive lines $\Delta\bar{\nu}$ in the spectrum is given by

$$\Delta\bar{\nu} = 2B = \frac{2h}{8\pi^2 Ic}$$

where, I is moment of inertia.

Thus, the separation $\Delta\bar{\nu}$ is inversely proportional to the moment of inertia of the rotor.

Hence, correct option is (b).

8. The rotational partition function for a diatomic molecule of moment of inertia I at a temperature T is given by

(a) $\frac{Ik_BT}{\hbar^2}$ (b) $\frac{2Ik_BT}{\hbar^2}$ (c) $\frac{3Ik_BT}{\hbar^2}$ (d) $\frac{Ik_BT}{2\hbar^2}$ **[GATE-2001]**

Soln. According to equipartition law of energy, the energy per degree of freedom is given by

$$E = \frac{1}{2} k_B T \qquad \text{... (i)}$$

Therefore, rotational energy of a diatomic molecule

$$= 2 \times \frac{1}{2} k_B T \qquad \text{... (ii)}$$

Also, rotational energy of a molecule is given by (For state J)

$$E_j = \frac{\hbar^2}{2I} J(J+1) \qquad \text{... (iii)}$$

From equation (ii) and (iii), we get

$$2 \times \frac{1}{2} k_B T = \frac{\hbar^2}{2I} J(J+1)$$

$$\Rightarrow \quad T = \frac{\hbar^2}{2I k_B} J(J+1)$$

$$\Rightarrow \quad J(J+1) = \frac{2I k_B T}{\hbar^2} \qquad \text{... (iv)}$$

Thus, partition function $= \frac{2I k_B T}{\hbar^2}$.

Hence, correct option is (b).

9. The allowed rotational energy levels of a rigid hetero-nuclear diatomic molecule are expressed as $\varepsilon_J = BJ(J+1)$, where B is the rotational constant and J is a rotational quantum number.

In a system of such diatomic molecules of reduced mass μ, some of the atoms of one element are replaced by a heavier isotope, such that the reduced mass is changed to 1.05μ. In the rotational spectrum of the system, the shift in the spectral line, corresponding to a transition $J = 4 \rightarrow J = 5$, is

[GATE 2007]

(a) 0.475B (b) 0.50 B (c) 0.95 B (d) 1.0 B

Soln. The allowed rotational energy

$$\varepsilon_j = BJ(J+1) \qquad \text{... (i)}$$

The wave number $(\bar{\nu})$ is given by

$$\bar{\nu} = 2B(J+1) \qquad \text{... (ii)}$$

where J is rotational quantum number and $B = \frac{h}{\pi^2 Ic}$ is rotational constant.

For the reduced mass μ the wave number corresponding to the transition $J = 4 \rightarrow 5$ is given by

$$\bar{\nu} = 2B(4+1) = 10B = 10\left(\frac{h}{8\pi^2 Ic}\right)$$

$$\Rightarrow \quad \bar{\nu} = \frac{10h}{8\pi^2(\mu r^2)c} \qquad \text{... (iii)}$$

For the reduced mass $\mu' = 1.05\,\mu$ and $J = 4 \rightarrow 5$ transition the wave number is given by

$$\bar{\nu}' = 2B'(4+5) = 10B' = 10\left(\frac{h}{8\pi^2 I'c}\right)$$

$$\Rightarrow \quad \bar{\nu}' = \frac{10h}{8\pi^2(\mu' r^2)c} = \frac{10h}{8\pi^2(1.05\,\mu r^2)c} \qquad \ldots (iv)$$

From equations (iii) and (iv), we get

$$\nu - \nu' = \frac{10h}{8\pi^2(\mu r^2)c}\left(1 - \frac{1}{1.05}\right) = 10B(1 - 0.9524)$$

$$\Rightarrow \quad \Delta\nu = 10B \times 0.0476 = 0.476B$$

Hence, correct option is (a).

10. Three consecutive absorption lines at 64.275 cm^{-1}, 77.130 cm^{-1} and 89.985 cm^{-1} have been observed in a microwave spectrum for a linear rigid diatomic molecule. The moments of inertia I_A and I_B are (I_A is with respect to the bond axis passing through the centre of mass and I_B is with respect to an axis passing through the centre of mass and perpendicular to bond axis) **[GATE 2008]**

(a) both equal to $\frac{\hbar^2}{12.855hc}$ gm cm^2 (b) zero and $\frac{\hbar^2}{12.855hc}$ gm cm^2

(c) both equal to $\frac{\hbar^2}{6.427hc}$ gm cm^2 (d) zero and $\frac{\hbar^2}{6.427hc}$ gm cm^2

Soln. The wave number of three consecutive lines are 64.275 cm^{-1}, 77.130 cm^{-1} and 89.985 cm^{-1}.

..... 89.985 cm^{-1} } 2 B
..... 77.130 cm^{-1} } 2 B
..... 64.275 cm^{-1}

Therefore, the difference in wave number

$$\Delta\bar{\nu} = 2B = 89.985 - 77.130$$

$$\Rightarrow \quad 2B = 12.855$$

$$\Rightarrow \quad 2 \times \frac{h}{8\pi^2 I_B^C} = 12.855$$

$$\Rightarrow \quad I_B = \frac{2h}{8\pi^2 C(12.855)} = \frac{\hbar^2}{12.855\,hC} \text{ gm } cm^2 \text{ and}$$

$I_A = 0$ ($\because$ r = 0, from the bond axis passing through the center of mass).

Hence, correct option is (a).

11. The molecular spectra of two linear molecules O-C-O and O-C-S are recorded in the microwave region. Which one of the following statement is correct?

(a) Both the molecules would show absorption lines
(b) Both the molecules woulb not show absorption lines
(c) O-C-O would show absorption lines, but not O-C-S.
(d) O-C-S would show absorption lines, but not O-C-O. **[GATE-2008]**

Soln. The CO_2 molecule do not have permanent dipole moment while COS have permanent dipole moment. Thus CO_2 molecule will not show absorption lines.

Hence, correct option is (d).

12. The far infrared rotational absorption spectrum of a diatomic molecule shows equivalent lines with spacing 20 cm^{-1}. The position of the first stokes line in the rotational Raman spectrum of this molecule is **[GATE-2011]**

(a) 20 cm^{-1} (b) 40 cm^{-1} (c) 60 cm^{-1} (d) 120 cm^{-1}

Soln. The line spacing in the infrared rotational absorption spectrum (2B) = 20 cm^{-1}

$\Rightarrow$ B = 10 cm^{-1}

Since, the distance of first stokes lines from Rayleigh line is 6B.

Therefore, the position of first stoke line in the rotational Raman spectrum = $6 \times 10\ cm^{-1} = 60\ cm^{-1}$.

Hence, correct option is (c).

13. The first stokes line of a rotational Raman spectrum is observed at 12.96 cm^{-1}. Considering the rigid rotor approximation, the rotational constant is given by **[GATE-2013]**

(a) 6.48 cm^{-1} (b) 3.24 cm^{-1} (c) 2.16 cm^{-1} (d) 1.62 cm^{-1}

Soln. The position of first stokes line of a rotational Raman spectrum = 12.96 cm^{-1}

i.e., 6B = 12.96 cm^{-1}

$\Rightarrow$ B = 2.16 cm^{-1}

Hence, the rotational constant B = 2.16 cm^{-1}.

Hence, correct option is (c).

14. In a rigid-rotator of mass *M*, if the energy of the first excited state is 1 *meV*, then the fourth excited state energy (in *meV*) is_____ **[GATE 2015]**

Sol. Since we know that energy of a rigid rotator

$$E = \frac{\hbar^2}{2I}(J)(J+1) \qquad \ldots (i)$$

where $J = 0, 1, 2, \ldots$

Energy of first excited state

$$(E_1) = \frac{\hbar^2}{2I}(I)(1+1) = 1\ meV \Rightarrow \frac{\hbar^2}{I} = 1\ meV \qquad \ldots (ii)$$

Energy of fourth excited state

$$E_4 = \frac{\hbar^2}{2I}4(4+1) = \frac{20}{2}\cdot\frac{\hbar^2}{I} = 10\frac{\hbar^2}{I} = 10 \times 1\ meV = 10\ meV$$

Hence, correct answer is 10.

15. In the microwave spectrum of identical rigid diatomic molecules, the separation between the spectral lines is recorded to be 0.7143 cm^{-1}. The moment of inertia of the molecule, in kg-m^2 is **[GATE - 2006]**

(a) 2.3×10^{-36} (b) 2.3×10^{-40} (c) 7.8×10^{-42} (d) 7.8×10^{-46}

Soln. The separation between spectral lines = 0.7143 cm^{-1}.

i.e., $2B = 0.7143$

$$\Rightarrow \quad B = \frac{0.7143}{2} \qquad \ldots (i)$$

The rotational constant $B = \frac{h}{8\pi^2 Ic}$

$$\Rightarrow \quad I = \frac{h}{8\pi^2 Bc} = \frac{6.6 \times 10^{-34} \times 2}{8 \times (3.14)^2 \times 0.7143 \times 3 \times 10^{10}} = 0.07809 \times 10^{-44} = 7.8 \times 10^{-46}\ kg\text{-}m^2.$$

Hence, correct option is (d).

16. Three values of rotational energies of molecules are given below in different units **[GATE - 2003]**

$P = 10\ cm^{-1}$

$Q = 10^{-23}$ joule

$R = 10^{4}$ MHz

Choose the correct arrangement in the increasing order of energy,

(a) P, Q, R (b) R, Q, P (c) R, P, Q (d) Q, R, P

Soln. The energy $P = 10\ cm^{-1}$

In units of joule, $P = 10 \times 6.6 \times 10^{-34} \times 3 \times 10^{10}$ joule

$\Rightarrow \quad P = 19.8 \times 10^{-23}$ joule ... (i)

The energy, $Q = 10^{-23}$ joule ... (ii)

The energy, $R = 10^{4}$ MHz

In units of joule, $R = 6.6 \times 10^{-34} \times 10^{4} \times 10^{6}$ joule

$\Rightarrow \quad R = 6.6 \times 10^{-24}$ joule

$\Rightarrow \quad R = 0.66 \times 10^{-23}$ joule ... (iii)

From equations (i), (ii) and (iii), the correct order of the increasing energy is R, Q, P.

Hence, correct option is (b).

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Chapter 7

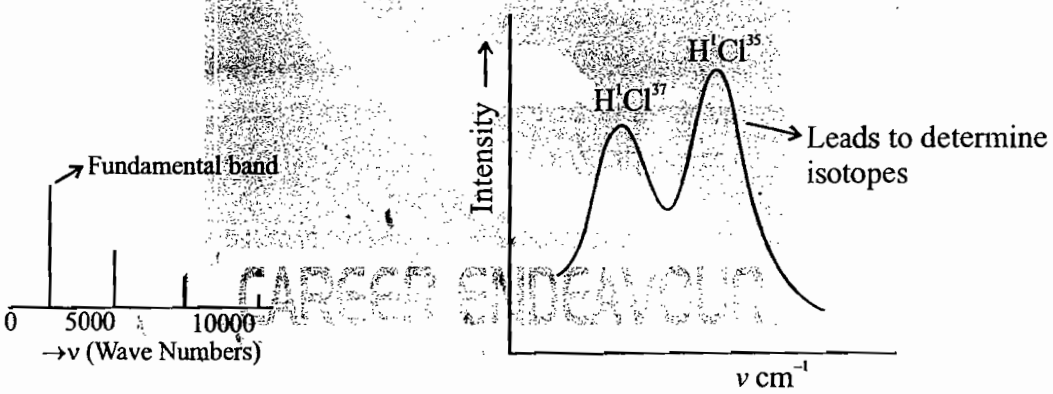
Vibrational Rotational Spectra

Salient features Vibrational Rotational Spectra:

Observed in absorption only for hetronuclear molecules which have permanent dipole moment in near infrared region $\left(10^0 \le \lambda \le 10^2\,\mu m \text{ and } E \sim 10^{-1}\,eV\right)$. The dipole moment interacts with the field of the light and starts oscillating and it leads to the spectrum.

H_2, N_2, O_2: Homonuclear molecules as they do not have permanent dipole moment does not show this spectra.

In practice, vibrational-rotational spectra of a molecule like HCl consists of an intense band, known as fundamental band and a number of weak bands called overtones at wave numbers approximately double triple of fundamental band.



[Fine structure of fundamental band for (HCl)

Vibrational spectra:

(a) The molecule as a harmonic oscillator :

The near infrared spectra are attributed to the vibrations of the nuclei in the diatomic molecule along the internuclear axis. The simplest possible assumption about the form of vibrations is to treat the molecule as a harmonic oscillator. The potential energy function under whose influence the nuclei vibrate is then parabolic, and of the form givne by

$$V(r) = \frac{1}{2}k(r - r_e)^2 = \frac{1}{2}kx^2$$

where, k is the force constant and x is displacement of the oscillator from the equilibrium position.

The Schrödinger wave equation describing this motion would be

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0$$

where, μ is the reduced mass of the oscillator. The allowed energies for the harmonic oscillator is

$$\boxed{E = \left(v + \frac{1}{2}\right) h\omega_{OSC} \text{ joules}}$$

where, $v = 0, 1, 2, 3, \ldots$, v is called the vibrational quantum number.

In terms of wave number,

$$\boxed{\varepsilon_v = \left(v + \frac{1}{2}\right) \bar{\omega}_{OSC} \text{ cm}^{-1}}$$

where, $\bar{\omega}_{OSC} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$.

The lowest vibrational energy, $v = 0$ is $\varepsilon_0 = \frac{1}{2}\bar{\omega}_{OSC} \text{ cm}^{-1}$.

The implication is that the diatomic molecule can never have zero vibrational energy; the atoms can never be completely at rest relative to each other. The quantity $\left(\frac{1}{2}\bar{\omega}_{OSC}\right) \text{ cm}^{-1}$ is known as the zero point energy; it depends only on the classical vibrational frequency and hence on the strength of the chemical bond and the atomic masses. The result is in accordance with the uncertainity principle, because if the oscillating particle were stationary, the uncertainity in its position would be $\Delta x = 0$ and its momentum uncertainity would then have to be infinite and a particle with $E = 0$ cannot have an infinitely uncertain momentum.

Selection rule :

The use of the Schrödinger equation leads to the selection rule as $\Delta v = \pm 1$. To this we must, of course add the condition that the vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation i.e. if the vibration involves a change in the dipole moment of the molecules. Thus, vibrational spectra will be observable only for molecules having permanent dipole moments, such as heteronuclear diatomic molecules like HBr, HCl etc. Homonuclear diatomic molecules like H_2, N_2, O_2 which necessarily have zero dipole moment for all internuclear distances fail to interact with radiation and so give no vibration spectra.

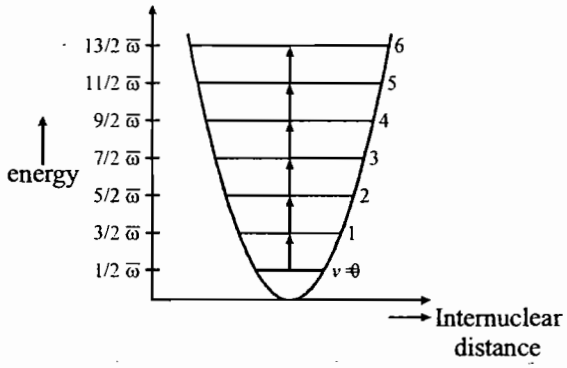
Applying the selection rule, we obtain

$\varepsilon_{v+1\to v} = \left(v + 1 + \frac{1}{2}\right)\bar{\omega}_{OSC} - \left(v + \frac{1}{2}\right)\bar{\omega}_{OSC} = \bar{\omega}_{OSC} \text{ cm}^{-1}$ for emission and for absorption, $\varepsilon_{v\to v+1} = \bar{\omega}_{OSC} \text{ cm}^{-1}$.

Thus the transition betweem two neighbouring states will give rise to the same energy change. Further, since the difference between energy levels expressed in cm^{-1} gives directly the wavenumber of the spectral line absorbed or emitted.

$$\bar{\nu}_{\text{spectroscopic}} = \varepsilon = \bar{\omega}_{OSC} \text{ cm}^{-1}$$

This again is obvious, if one considers the mechanism of absorption or emission in classical terms. In absorption, for instance, the vibrating molecule will absorb energy only from radiation with which is can coherently interact and this must be radiation of its own oscillation frequency.

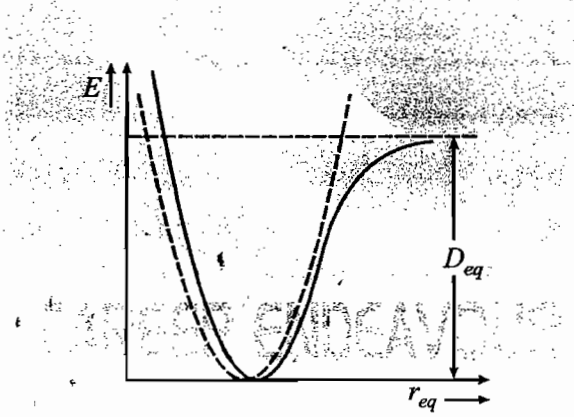


The vibrational spectrum is observed to consist of a single band at $\bar{\omega}_{OSC}$ cm^{-1}. The observation of a very intense band in the infrared spectrum thus leads to the conclusion that is is a vibrational spectrum, the nuclei carrying out harmonic vibrations along the internuclear axis.

(b) The Anharmonic oscillator :

Real molecules do not obey exactly the laws of simple harmonic oscillation, real bonds, although elastic are not so homogeneous as to obey Hooke's law. If the bond between the atoms is stretched, for instance, there comes a point at which it will break the molecule dissociates into atoms.

The figure given below shows, diagrammatically, the shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.



A pure empirical expression which fits this curve to a good approximation was derived by morse and is called the morse function:

$$E = D_{eq}\left[1-\exp\left\{a(r_{eq}-r)\right\}\right]^2$$

where, a is a constant for a particular molecule and D_{eq} is the dissociation energy. To a first approximation, the potential energy $V(r)$ can be expanded through the Taylor series to get

$$V(r) = \frac{1}{2!}\left\{\frac{\partial^2 V(r)}{\partial r^2}\right\}_{r=r_e}(r-r_e)^2 + \frac{1}{3!}\left\{\frac{\partial^3 V(r)}{\partial r^3}\right\}_{r=r_e}^{(r-r_e)^3}$$

$$= f(r-r_e)^2 - g(r-r_e)^3 = fx - gx^3 \quad [\text{where, } g \ll f]$$

On substituting this $V(r)$ in the schrö equation and solving the energy eigen values of the anharmonic oscillator is found to be

$$E_v = h\omega_e\left(v+\frac{1}{2}\right) - h\omega_e x_e\left(v+\frac{1}{2}\right)^2$$

or in terms of wave numbers (cm^{-1})

$$\boxed{\varepsilon_v = \left(v+\frac{1}{2}\right)\bar{\omega}_e - \left(v+\frac{1}{2}\right)^2 \bar{\omega}_e x_e \text{ cm}^{-1}} \quad \text{... (i)}$$

where, $v = 0, 1, 2, 3, \ldots$ and $\bar{\omega}_e$ is an oscillation frequency [which will be described later], and x_e is the corresponding an harmonicity constant which for band stretching vibrations, is always small and positive ($\approx +0.01$) so that vibration levels crowd more closely together with increasing v.

If we rewrite the ε_v for anharmonic oscillator, as :

$$\varepsilon_v = \bar{\omega}_e\left\{1 - x_e\left(v+\frac{1}{2}\right)\right\}\left(v+\frac{1}{2}\right)$$

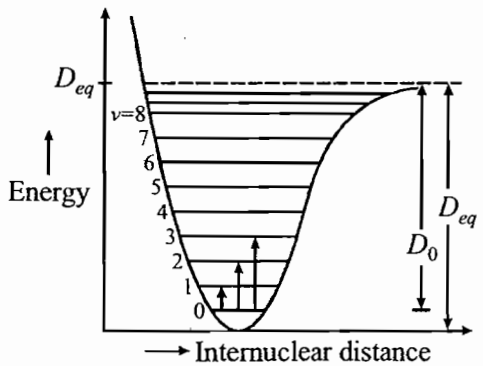
and compare with the energy levels of harmonic oscillator, we can write $\bar{\omega}_{osc} = \bar{\omega}_e\left\{1 - x_e\left(v+\frac{1}{2}\right)\right\}$.

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency whicl decreases steadily with increasing v. If we consider the hypothetical energy state obtained by putting $v = -\frac{1}{2}$ (at which according to equation (i), $\varepsilon_v = 0$) the molecule would be at the equilibrium point with zero vibration energy. Its oscillation frequency would be $\bar{\omega}_{osc} = \bar{\omega}_e$.

Thus we define $\bar{\omega}_e$ as the (hypothetical) equilibrium oscillation frequency of the anharmonic system the frequenc for infinitely small vibrations about the equilibrium point. Thus in the ground state ($v = 0$) we would have :

$$\bar{\omega}_0 = \bar{\omega}_e\left(1 - \frac{1}{2}x_e\right) \text{ cm}^{-1} \text{ and } \varepsilon_0 = \frac{1}{2}\bar{\omega}_e\left(1 - \frac{1}{2}x_e\right) \text{ cm}^{-1}$$

Thus the zero point energy differs slightly from that for the harmonic oscillator.



Selection Rule :

The selection rules for the anharmonic oscillator are found to be $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$. Hence, all types transitions from any lower vibrational level to any of the higher vibrational levels are allowed. The Transitic corresponding to $\Delta v > 1$ do take place. This, intum, is attributed to the fact that the dipole moment of molecule is not strictly linear with respect to the internuclear distance.

Since only the lowest level is thickly populated and because the population decreases very rapidly with increasing v only a few transitions from the lowest vibrational level ($v = 0$) to the next nearest vibrational levels are actually observed at room temperature.

(i) $v = 0 \rightarrow v = 1, \quad \Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$

$$\Rightarrow \quad \boxed{\Delta\varepsilon = \bar{\omega}_e(1 - 2x_e)\,\text{cm}^{-1}}$$

This transition is found to be the most intense and is known as the fundamental absorption.

(ii) $v = 0 \rightarrow v = 2, \quad \Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0}$

$$\Rightarrow \quad \boxed{\Delta\varepsilon = 2\bar{\omega}_e(1 - 3x_e)\,\text{cm}^{-1}}$$

This transition is found to have a poor intensity and is known as the "first overtone".

(iii) $v = 0 \rightarrow v = 3, \quad \Delta\varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0}$

$$\Rightarrow \quad \boxed{\Delta\varepsilon = 3\bar{\omega}_e(1 - 4x_e)\,\text{cm}^{-1}}$$

This transition is found to have negligible intensity and is known as the "second overtone".
The higher overtones are too weak to be realised experimentally.
The transitions from $v = 1$ to the higher levels are not observed unless the temperature of the sample is high, or if the vibration has a particularly low frequency. This is due to the fact that the population in $v = 1$ level is negligible at room temperature and it becomes appreciable only at higher temperatures. The transition is

(iv) $v = 1 \rightarrow v = 2, \quad \Delta v = \pm 1$

$$\Rightarrow \quad \boxed{\Delta\varepsilon = \bar{\omega}_e(1 - 4x_e)\,\text{cm}^{-1}}$$

This transition is very weak and it will be found close to and at slightly lower wave numbers than the fundamental such weak absorptions are usually called "hot bands". Since a high temperature is one condition for their occurence. Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

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Dissociation energy of a diatomic molecule

The vibrational energy of a molecule increases with increase in the vibrational quantum number (v). Eventually a stage is reached where vibrational energy is quite sufficient to break the molecule into atoms. This energy is known as the "dissociation energy" of the diatomic molecule. Thus at the dissociation stage of the molecule, the vibrational energy has a maximum value.

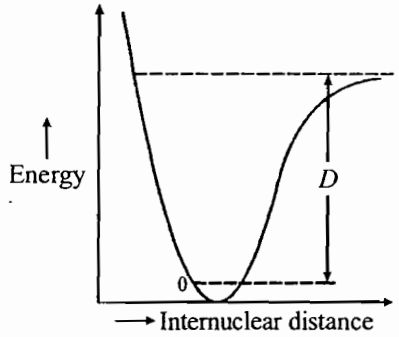
The value of vibrational quantum at this stage may be determined by $\frac{\partial \varepsilon_v}{\partial v} = 0$.

$$\therefore \quad \frac{\partial \varepsilon_v}{\partial v} = 0 = \bar{\omega}_e\left\{1 - \left(v_{\max} + \frac{1}{2}\right)x_e\right\} + \left(v_{\max} + \frac{1}{2}\right)\bar{\omega}_e(-x_e)$$

$$\text{or} \quad 1 - 2\left(v_{\max} + \frac{1}{2}\right)x_e = 0 \quad \text{or} \quad v_{\max} = \frac{1}{2x_e} - \frac{1}{2}$$

Substituting $v_{\max}$ in energy equation, we get, $\varepsilon_{\max} = \frac{\bar{\omega}_e}{4x_e}\,\text{cm}^{-1}$

This will represent the dissociation energy of the molecule with respect to the bottom of the potential energy diagram. The true dissociation energy, however, will be given by



$$D = \varepsilon_{max} - \varepsilon_0 \Rightarrow D = \frac{\bar{\omega}_e}{4x_e} - \frac{1}{2}\bar{\omega}_e\left(1 - \frac{1}{2}x_e\right)$$

The obtained value of dissociation energy will not be accurate one since the energy equation (i) is obtained as an approximate solution of the schrödinger equation. More precise solution, in fact, includes the cubic, quadratic etc. terms in $\left(v + \frac{1}{2}\right)$ with anharmonicity constant y_e, z_e etc. The magnitudes of y_e, z_e etc. diminish very rapidly. Though these higher terms are negligible for the small values of v, they become important at large v.

- The force constant for anharmonic oscillator may be calculated from the equation $k = 4\pi^2\bar{\omega}_e^2 c^2 \mu$.
- The relative populations of energy levels as given by Boltzman equation is $N_i = N_0 \exp\left(-\frac{\Delta E_i}{kT}\right)$, where, ΔE_i the energy difference between the i^{th} level and the zeroth level. The relative population i.e. the term N_i/N_0 depends on the ratio $\Delta E_i/kT$. From the experimental data on the vibrational spectra, it is found that in most diatomic molecules $\Delta E_{0\to1}$ is much higher than the thermal energy kT.

(c) Vibration rotation spectra :

Pure vibrational spectra are observed only in liquids where interactions between adjacent molecules inhibit rotation. Because the excitation energies involved in molecular rotation are much smaller than those involved in vibration, the freely moving molecules in a gas or vapour nearly always are rotating, regardless of their vibrational state. The spectra of such molecules do not show isolated lines corresponding to each vibrational transition, but instead a large number of closely spaced lines due to transitions between the various rotational states of one vibrational level and the rotational states of the other. In spectra obtained using as spectrometer with inadequate resolution, the lines appear as a broad streak called a "vibration rotation" band.

(i) The diatomic vibrating rotator (with born oppenheiver approximation) :

A typical diatomic molecule has rotational energy separations of 1-10 cm^{-1}, while the vibrational energy separations are nearly 3000 cm^{-1}. Since the energies of two motions are so different we may, as a first approximation, consider that a diatomic molecule can execute rotations and vibration quite independently. This, which we shall call the Born oppenheimer approximation, is tantamount to assuming that the combined rotational vibrational energy is simply the sum of the separate energies :

$$E_{total} = E_{rot} + E_{vib} \text{ (Joules)}; \quad \varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib} \quad (cm^{-1})$$

Taking the separate expression $\varepsilon_{rot} + \varepsilon_{vib}$ respectively, we have

$$\varepsilon_{J,v} = BJ(J+1) - DJ^2(J+1)^2 + \left(v + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \frac{1}{2}\right)^2\bar{\omega}_e \ cm^{-1}$$

Initially, we shall ignore small centrifugal distortion constant D, as retention of D would have only a very minor effect on the spectrum.

$$\because \quad \varepsilon_{\text{total}} = \varepsilon_{J,v} = BJ(J+1) + \left(v+\frac{1}{2}\right)\bar{\omega}_e - x_e\left(v+\frac{1}{2}\right)^2 \bar{\omega}_e$$

Selection Rule :

The selection rules for the combined motions are the same as those for each separately, therefore we have $\Delta v = \pm 1, \pm 2$ etc. and $\Delta J = \pm 1$

Strictly speaking we may also have $\Delta v = 0$ but this corresponds to the purely rotational transitions. Note carefully, however, that a diatomic molecule, except under very special and rare circumstances, maynot have $\Delta J = 0$; in other words a vibrational change must be accompanied by a simultaneous rotational change.

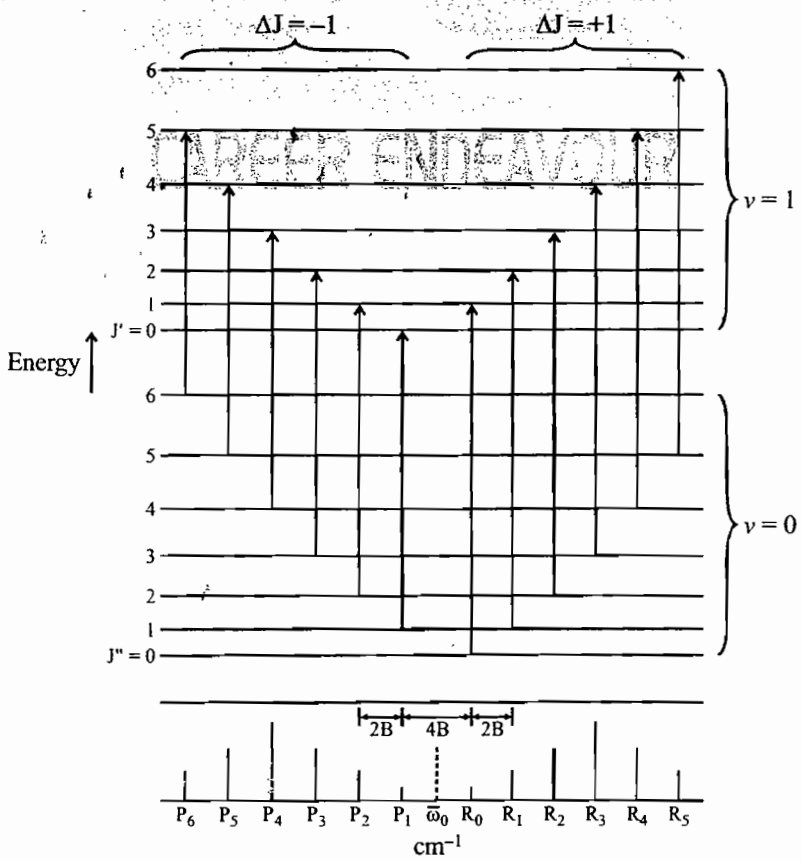
Rotational vibrational transition :

An analytical expression for the spectrum may be obtained by applying the selection rules to the energy levels. Considering only the $v = 0 \rightarrow v = 1$ transitions we have in general

$$\Delta\varepsilon_{J,v} = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0} = BJ'(J'+1) + \frac{3}{2}\bar{\omega}_e - \frac{9}{4}x_e\bar{\omega}_e - \left\{BJ''(J''+1) + \frac{\bar{\omega}_e}{2} - \frac{1}{4}x_e\bar{\omega}_e\right\}$$

Here the rotational quantum numbers in $v = 0$ state are designated as J'' and in the $v = 1$ state as J'. Note that the rotational constant B is taken to be the same for all J and v (a consequence of the Born Oppenheimer approximation); the separation between two levels if given J is the same in $v = 0$ and $v = 1$ states.

The above expression can be written as $\boxed{\Delta\varepsilon_{J,v} = \bar{\omega}_0 + B(J'-J'')(J'+J''+1)\,\text{cm}^{-1}}$, where $\bar{\omega}_0 = \bar{\omega}_e(1-2x_e)$.



Some transitions be the rotational-vibrational energy level of a diatomic molecule. Remember that the rotational levels J'' are filled to varying degrees in any molecular population, so the transitions shown will occur with varying intensities. This is indicated schematically in the spectrum above.

Since, $\Delta\varepsilon_{J,v} = \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1)\ \text{cm}^{-1}$

We have,

1. $\Delta J = +1$ that is $J' = J'' + 1$ [R-branch]

So, $\boxed{\Delta\varepsilon_{J,v} = \bar{\omega}_0 + 2B(J'' + 1)\,\text{cm}^{-1}}$ ... (a)

where, $J'' = 0, 1, 2, ...$

2. $\Delta J = -1$ that is $J' - J'' = -1$, hence [P-branch]

$\boxed{\Delta\varepsilon_{J,v} = \bar{\omega}_0 - 2B(J' + 1)\,\text{cm}^{-1}}$ ... (b)

where, $J' = 0, 1, 2, ...$

These two expressions may conveniently be combined into

$\boxed{\Delta\varepsilon_{J,v} = \bar{\nu}_{\text{spect}} = \bar{\omega}_0 + 2Bm\,\text{cm}^{-1}}$ ... (c)

where, $m = \pm 1, \pm 2, ...$

and $\bar{\omega}_0 = \bar{\omega}_e(1 - 2x_e)$

where, m replacing $J'' + 1$ in equation (a) and $J' + 1$ in equation (b) has positive values for $\Delta J = +1$ and is negative if $\Delta J = -1$. Note particularly that m cannot be zero since this would imply values of J' or J'' to be -1. The frequency $\bar{\omega}_0$ is usually called the band origin or band center.

Equation (c) then represents the combined vibration-rotation spectrum. Evidently it will consist of equally spaced lines (spacing = $2B$) on each side of the band origin $\bar{\omega}_0$, but since $m \neq 0$, the line at $\bar{\omega}_0$ itself will not appear. Lines to the low-frequency side of $\bar{\omega}_0$, corresponding to negative m (that is $\Delta J = -1$) are referred to as "P-branch", while those of the high frequency side (m positive, $\Delta J = +1$) are called the "R-branch". It is readily shown that the inclusion of the centrifugal distortion constant D leads to the following expression for the spectrum:

$\boxed{\Delta\varepsilon = \bar{\nu}_{\text{spect}} = \bar{\omega}_0 + 2Bm - 4Dm^3}\ \text{cm}^{-1},\ m = \pm 1, \pm 2, \pm 3, ...$

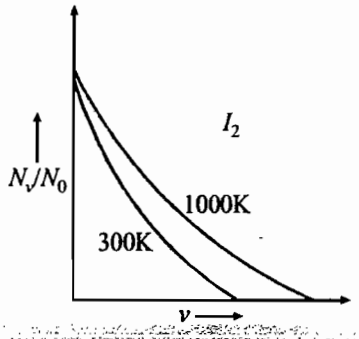
However, since B is approximately 10 cm^{-1} or less, while D is only some 0.01 percent of B. Since a good infrared spectrometer has a resolving power of about 0.5 cm^{-1}, it is obvious that D is negligible to a very high degree of accuracy.

The anharmonicity factor on the other hand is not negligible. It affects not only the position of the band origin. Since $\bar{\omega}_0 = \omega_e(1 - 2x_e)$, but by extending the selection rules to $\Delta v = \pm 2, \pm 3$ etc. also allows the appearence of overtone band having identical rotational structure.

Thermal distribution of vibrational and rotational levels :

Vibrational levels : According to Maxwell's Boltzman distribution law, the number of molecules in vth state, N_v relative to that in the lowest state, N_0 is given by $N_v = N_0\, e^{-(\varepsilon_v - \varepsilon_0)/k_B T}$, where $\varepsilon_v = \bar{\omega}_e\left(v + \frac{1}{2}\right) - \bar{\omega}_e x_e^-\left(v + \frac{1}{2}\right)^2$

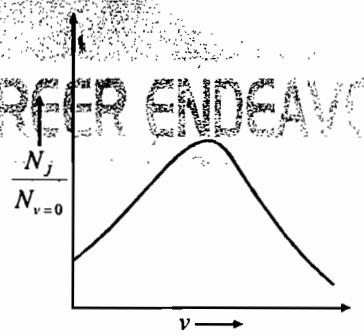
The figure here is a graph $\left(\frac{N_v}{N_0}\right)$ and the vibrational quantum number v for I_2 molecules at temperatures 300K and 1000K. It is seen that at room temperature the population of higher vibrational levels is very small compared to that of the lowest $v = 0$ level. It is still smaller, even at higher temperatures, for lighter molecules H_2, HCl, N_2 etc. The $v = 1$ level has an appreciable population only in the heaviest diatomic molecules which have smaller vibrational quanta.



Rotational levels : Let $N_{v=0}$ be the total number of molecules in the lowest vibration state ($v = 0$). These molecules will be distributed among the rotational levels associated with this vibrational state according as

$$N_J = \frac{N_{v=0}(2J+1)e^{-BJ(J+1)hc/kT}}{\sum_{J=0}^{\infty}(2J+1)e^{-BJ(J+1)hc/kT}}$$

So, $\frac{N_J}{N_{v=0}} = \frac{hcB}{kT}(2J+1)e^{-BJ(J+1)hc/kT}$



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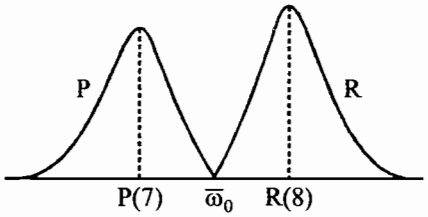
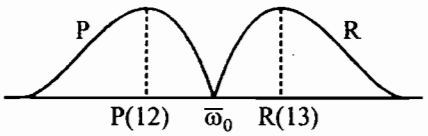
It is seen that as J increases, the population first rises to a maximum and then decreases. The value of J at which population is maximum is obtained by putting $\frac{d}{dJ}\left(\frac{N_J}{N_{v=0}}\right) = 0$.

$$\therefore\ J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

combined intensity distribution in the rotational structure of $0 \rightarrow 1$ vibrational band of CO in absorption at 300K and 1000K. We see that intensity is zero at the band origin $\bar{\omega}_0$, increases with increasing J on either side of it, reaches a maximum and then slowly decreases. In both R and P branches the maximum occurs at about

the same value of J at which the population is maximum. However on whole the R branch is stronger than the P-branch. (Reverse is the case in an emission band).





As the temperature of the molecular gas is raised, the following effects are observed:

(i) The band extends on both sides because more lines in each branch appear.

(ii) The intensity maxima in both branches move farther away from $\bar{\omega}_0$, that is occur at higher J values.

(iii) The height of the intensity maxima decreases.

(iv) The inequality between the intensities of the two branches becomes less marked.

Applications of vibrational rotational spectrum :

The vibration rotation spectrum can be utilized to determine all those molecular parameters which can be determined separately from the pure vibration and pure rotationa spectra. The location of band center corresponding to the transition ($v'' = 0 \rightarrow v' = 1$) (the fundamental transition) and $v'' = 0 \rightarrow v' = 2$ (the first overtone) helps in providing the values $\bar{\omega}_e$ and x_e and hence the value of force constant. The separation of lines in either P branch or R branch provides the value of $2B$ and hence the values of moment of inertia and the bond length. The approximate value of parameter B can even be evaluated if the rotational lines are not resolved i.e. from the spectrum shown in figure below.

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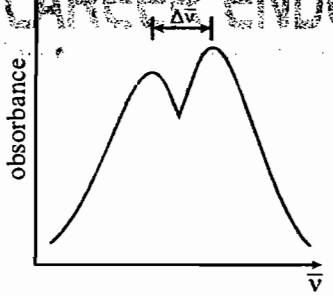


Here under much poorer resolution the rotational fine structure is blurred out to an envelope. The quantum number of the rotational level having maximum population is given by

$$J = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

This quantum level will produce the maximum intensity of the rotational transition.

Now, since $m = \pm(J+1)$, we have $m_{max} = \pm\left(\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}\right)$ and hence the maxima of P and P branches will be located at $\bar{\nu}_{\text{max intensity}} = \bar{\omega}_0 \pm \left(\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}\right)2B$, where $\bar{\omega}_0 = \bar{\omega}_e(1-2x_e)$, where (+) and (–) signs refer to the R and P branches, respectively. The sparation between the two maxima, $\Delta\bar{\nu}$ is given by

$$\Delta\bar{\nu} = 4B\left(\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}\right) = \sqrt{\frac{8kTB}{hc}} + 2B$$

or, since B is small compared to $\Delta\bar{\nu}$, we can write $\Delta\bar{\nu} \simeq \sqrt{\frac{8kTB}{hc}}$.

$$\therefore \quad \boxed{B \approx \frac{hc(\Delta\bar{\nu})^2}{8kT}\text{cm}^{-1}}$$

Note: The Q branch, when it occurs, consists of lines corresponding to $\Delta J = 0$. Generally, these transitions are forbidden, except for the molecules like NO, which have orbital angular momentum about their axes.

(2) The diatomic vibrating rotator (with breakdown of Born oppenheimer approximation) :

So, far we have assumed that vibration and rotation can proceed quite independently of each other. A molecules vibrates some 10^3 times during the course of a single rotation, however, so it is evident that the bond length (and hence B) also changes continually during the rotation. If the vibration is simple harmonic the mean band length will be the same as the equilibrium bond length and it will not vary with vibrational energy.

In case of anharmonic oscillator the increase in vibrational energy will lead to an increase in average bond length and the rotational constant (B) then varies even more with vibrational energy.

Also in a given vibrational state, the intermolecular distance and hence the rotational constant B is changing during the vibration. So mean value of rotational constant in a given vibration state, namely,

$$B_\nu = \frac{\hbar}{8\pi^2\mu c}\left(\frac{1}{r^2}\right)_\nu$$

where, $\left(\frac{1}{r^2}\right)_\nu$ is the mean value of $\frac{1}{r^2}$ in vibration state ν during the vibration.

It can be shown that $B_\nu = B_e - \alpha_e\left(\nu + \frac{1}{2}\right)$, where α_e is a constant depending upon the shape of the potential curve ($\alpha_e \ll B_e$), and B_e is the rotational constant corresponding to the separation r_e at the minimum of the potential curve $\left(B_e = \frac{h}{8\pi^2 c\mu r_e^2}\right)$.

The selection rules are the same as for those systems individually, that is $\Delta\nu = \pm1, \pm2, \pm3, \ldots$; $\Delta J = \pm1$.

$$\varepsilon_{J,\nu} = \bar{\omega}_e\left(\nu + \frac{1}{2}\right) - \bar{\omega}_e x_e\left(\nu + \frac{1}{2}\right)^2 + B_\nu J(J+1)$$

Here we restrict our discussion to the fundamental vibrational change, i.e. the change $v = 0 \rightarrow v = 1$ and we may take the respective B values as B_0 and B_1 with $B_1 < B_0$.

For this transition:

$$\Delta\varepsilon = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0} = \bar{\omega}_0 + B_1 J''(J'+1) - B_0 J''(J''+1)\ \text{cm}^{-1}$$

where, as before, $\bar{\omega}_0 = \bar{\omega}_e(1-2x_e)$, we then have the two cases:

(i) $\Delta J = +1, J' = J''+1 = \bar{\omega}_0 + B_1(J''+1)(J''+1+1) - B_0(J''+1-1)(J''+1)$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\omega}_0 + (B_1 + B_0)(J''+1) + (B_1 - B_0)(J''+1)^2\ \text{cm}^{-1}\quad (J'' = 0, 1, 2, ...)$$

(ii) $\Delta J = -1,\ J'' = J'+1$

$$\Delta\varepsilon = \bar{\nu}_p = \bar{\omega}_0 - (B_1 + B_0)(J'+1) + (B_1 - B_0)(J'+1)^2\ \text{cm}^{-1}$$

$$\Delta\varepsilon = \bar{\omega}_0 + B_1 J'(J'+1) B_1(J'+1-1)(J'+1) - B_0(J'+1)(J'+1+1),\quad (J' = 0, 1, 2, ...)$$

These two equations can be combined into the expression:

$$\boxed{\bar{\nu}_{P,R} = \bar{\omega}_0 + (B_1 + B_0)m + (B_1 - B_0)m^2\ \text{cm}^{-1}} \quad \text{... (ii)}$$

$(m = \pm 1, \pm 2, ...)$

where positive m values refers to the R branch and negative to P.

$m = +1, +2, +3, +4, ...$ R-branch

$m = -1, -2, -3, -4, ...$ P-branch

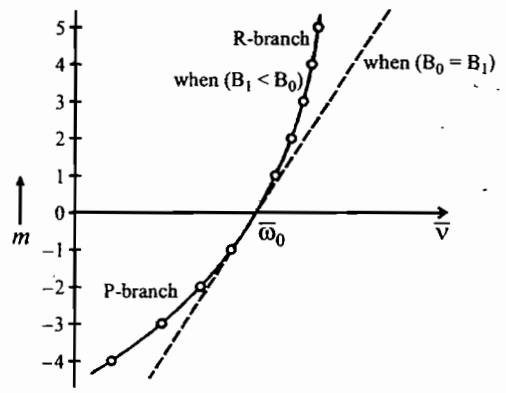
If we neglect vibration rotation interaction $(B_1 = B_0 - B)$

So, $\boxed{\bar{\nu}_{P,R} = \bar{\omega}_0 + 2Bm}$ $m = \pm 1, \pm 2, ...$ ... (iii)

Since $B_1 < B_0$ the last term in equation (ii) is always negative, irrespective of sign of m and the effect on the spectrum of a diatomic molecule is to crowd rotational lines more closely together on increasing m on the R branch side, while the P branch lines become more widely spaced as (negative) m increases. Normally B_1 and B_0 differ only slightly and the effect is marked only for high m values. The exact equation for equation (ii) is a parabola and (iii) is a straight line. Both of them are plotted as

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right)$$

$$B_1 < B_0$$

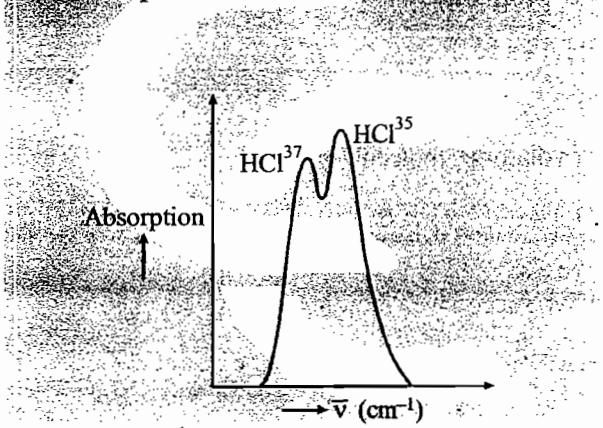


Since the constant α_e is very small, the difference $(B_1 - B_0)$ is also very small. Hence the curve is only slightly deviated from the straight line. This is why the vibration rotation bands show a very poor tendency of head formation.

Further, for vibration-rotation bands, both the involved vibrational levels belong to the same electronic state. Therefore the rotational constant for the upper vibrational state (B_1) is always smaller than that for the lower vibrational state B_0(since $r_1 > r_0$). In other words, $(B_1 - B_0)$ is always negative, though small. Hence, the line spacing decreases as m takes on increasing positive values. This means that the tendency of head formation is always seen in the R-branch. Conversely, the degradation of band is observed in the P-branch. This may be expressed by saying that rotation vibration bands are always degraded towards the lower wave-number side or higher wavelength side i.e., towards the red.

Use of rotational vibrational spectrum:

(i) Among the interesting results that can be obtained from analysis of vibrational states and spectra are the relative abundance of nuclear isotopes. The frequency of vibration $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, depends on the masses of the atoms in the molecule through the reduced mass μ. If in a sample of HCl molecules, for example, the isotopes Cl^{35} and Cl^{37} are each present, then the vibration frequencies and resulting energy levels will be slightly different for the two types of molecule. Their spectral lines, consequently, will be shifted with respect to one another and form a measurement of spectral intensities, we can obtain the relative abundance of the isotopes Cl^{35} and Cl^{37}.



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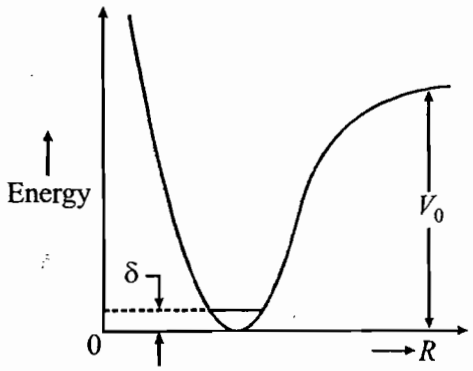
(ii) In a somewhat related way, we can obtain experimental evidence for the finite zero point energy of an oscillator. Consider the molecules D_2, H_2 and HD in which D stands for a Deuterium atom. Because the electrical forces are identical curve V(R) as illustrated in the figure below.



The energy required to dissociate the molecule is $E_d = V_0 - \delta$. If the ground state energy δ were zero, then the dissociation energies would be the same. i.e., $E_d = V_0$, for type of molecule. Quantum theory gives a finite

zero point energy, namely $\delta = \frac{1}{2}h\nu_0$. However, becuase the reduced mass μ enters the formula for ν_0, δ has a different value of each type of molecule so that their dissociation energies should differ. In fact, with $\mu_{D_2} = 2\mu H_2$ and $\mu_{HD} = \left(\frac{4}{3}\right)\mu H_2$. We can predict the difference, and we find that the observed dissociation energies differ exactly as predicted, thereby verifying the existence of a zero point energy.

SOLVED PROBLEMS

1. The force constant of the bond in CO molecule is 1870 N/m. Calculate the frequency of vibrational of the molecule and spacing between its vibrational energy levels in eV. Given that reduced mass of $CO = 1.14\times10^{-28}\ kg$, $h = 6.63\times10^{-27}$ erg-sec and $1\,eV = 1.60\times10^{-26}\ erg$.

Soln. Frequency of vibration of the CO molecule is

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\times3.14}\sqrt{\frac{1870\ N/m}{1.14\times10^{-26}\ kg}}$$

$$= 6.45\times10^{13}\ /\text{sec}$$

The vibrational energy of a diatomic molecule is

$$E_v = h\nu_{osc}\left(v+\frac{1}{2}\right) \qquad v = 0,1,2.....$$

The separation between two successive vibrational energy level is:

$$\Delta E = E_{v+1} - E_v$$

$$= h\nu_{osc}\left(v+\frac{3}{2}\right) - h\nu_{osc}\left(v+\frac{1}{2}\right)$$

$$= h\nu_{osc}$$

$$= \left(6.63\times10^{-27}\ erg-\text{sec}\right)\left(6.45\times10^{13}\ s^{-1}\right)$$

$$= 42.76\times10^{-14}\ erg$$

$$= \frac{42.76\times10^{-14}}{1.60\times10^{-12}} = 26.\times10^{-2}\ eV$$

2. In the near infra-red spectrum of HCl molecule there is a single intense band at $2885.9\ cm^{-1}$. Assuming that it is due to the transition between vibrational levels, show that the force constant k is $4.8\times10^5\ dyne/cm$. (Given: $\mu = 1.68\times10^{-24}\ gm$).

Soln. The wave number of the fundamental vibrational band is ω, the vibrational constant of the molecule. Thus

$$\omega = 2885.9\ cm^{-1}$$

But $\omega = \frac{\nu_{osc}}{c}$, where ν_{osc} is the fundamental frequency of vibration.

Now,

$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, where k is the force constant.

And μ is the reduced mass of te molecule.

$\therefore \quad k = 4\pi^2 \mu \nu_{osc}^2 = 4\pi^2 \mu \omega^2 c^2$ ... (1)

The reduced mass of H^1Cl^{35} is given by

$$\mu = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

$$= \frac{1\times 35}{1+35} M_H = \frac{35}{36} \times 1.68\times 10^{-24}\ gm = 1.63\times 10^{-24}\ gm$$

Substituting the values of μ, ω & c in equation (1), we get

$$k = 4\times (3.14)^2 \times \left(1.63\times 10^{-24}\ gm\right)\times \left(2885.9\ cm^{-1}\right)^2 \times \left(3\times 10^{10}\ cm\ \sec^{-1}\right)^2$$

$$= 4.8\times 10^5\ dyne/cm$$

3. Calculate the amplitude of the vibrations in the $v = 0$ level of the molecule ω which has a stiff bond of $18.7\times 10^5\ dyne/cm$. $\left(h = 6.63\times 10^{-27}\ erg - s\right)$

Soln. Given: $k = 18.7\times 10^5\ dyne/cm$

Let x_0 be the maximum displacement (amplitude) from the equilibrium position. The potential energy at $x = x_0$ is equal to the vibrational energy to the $v = 0$ state.

i.e.

$$\frac{1}{2} k x_0^2 = \frac{1}{2} h\nu_{osc}$$

$$\therefore \quad x_0 = \sqrt{\frac{h\nu_{osc}}{k}} \quad \text{... (1)}$$

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Now, $\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

where μ is the reduce mass of the molecule.

The reduced mass of the $C^{12}O^{16}$ molecule is given by

$$\mu = \frac{(12\times 16)/\left(6.023\times 10^{23}\right)^2}{(12+16)/6.023\times 10^{23}} = 1.14\times 10^{-23} g = 1.14\times 10^{-26} kg.$$

$$\therefore \quad \nu_{osc} = \frac{1}{2\times 3.14}\sqrt{\frac{18.7\times 10^5\ dyne/cm}{11.4\times 10^{-24}\ gm}}$$

$$= 6.45\times 10^{13}\ \sec^{-1}$$

Putting this value in equation (1), we get

$$x_0 = \sqrt{\frac{\left(6.63\times 10^{-27}\ erg - \sec\right)\left(6.45\times 10^{18}\ \sec^{-1}\right)}{18.7\times 10^5\ dyne/cm}} = 4.78\times 10^{-10}\ cm = 4.78\times 10^{-2}\ \mathring{A}$$

4. The values of ω_e 4395, 3817 and 3118 cm^{-1} for H_2, HD and D_2 molecules respectively. Calculate their approximate zero-point energies in Kcal/mole. The values of $\omega_e x_e$ are 118, 95 and 64 cm^{-1} for the same molecules. Calculate the exact zero point energies.

Soln. The approximate term value for the molecule are given by

$$G(v) = \omega_e\left(v+\frac{1}{2}\right)$$

The zero-point energy corresponding to $v = 0$ is,

$$\therefore \quad G(0) = \frac{1}{2}\omega_e$$

For $H_2, \omega_e = 4395\, cm^{-1}$

$$\therefore \quad G(0) = \frac{1}{2}\times 4395 = 2197.5\ cm^{-1}$$

$$1\, cm^{-1} = 2.86\times 10^{-3}\ k\ cal/mole$$

$$\therefore \quad G(0) = 2197.5\left(2.86\times 10^{-3}\right)$$

$$= 6.28\ k\ cal/mole$$

Similarly, for HD, $G(0) = 5.45\ kcal/mole$

for D_2, $G(0) = 4.46\ kcal/mole$

Now,

The more accurate term values are given by

$$G(v) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2$$

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$

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For $H_2, \omega_e = 4395\, cm^{-1}$ & $\omega_e x_e = 118\, cm^{-1}$

$$\therefore \quad G(0) = \frac{1}{2}\times 4395 - \frac{1}{4}\times 118$$

$$= 2197.5 - 29.5 = 2168\ cm^{-1}$$

$$= 2168\times\left(2.86\times 10^{-3}\right) = 6.20\ kcal/mole$$

Similarly,

For HD, $G(0) = 5.39\ kcal/mole$

$D_2, G(0) = 4.41\ kcal/mole$

5. The fundamental band for CO is centered at $2143.3\ cm^{-1}$ and the first overtone at $4259.7\ cm^{-1}$. calculate $\omega_e, \omega_e x_e$, the vibrational frequency and the simple harmonic force constant.

Soln. The vibrational terms of a diatomic molecule are given by

$$G(v) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2$$

$$G(0)=\frac{1}{2}\omega_e-\frac{1}{4}\omega_e x_e$$

$$G(1)=\frac{3}{2}\omega_e-\frac{9}{4}\omega_e x_e$$

$$G(2)=\frac{5}{2}\omega_e-\frac{25}{4}\omega_e x_e$$

For the wave number of fundamental band $1\rightarrow 0$,
We have

$$\nu=G(1)-G(0)$$

$$=\omega_e-2\omega_e x_e=2143.3\ cm^{-1} \qquad \ldots(1)$$

For the first overtone band $2\rightarrow 0$, We have

$$\nu=G(2)-G(0)$$

$$2\omega_e-6\omega_e x_e=4259.7\ cm^{-1} \qquad \ldots(2)$$

Solving equation (1) and (2), we get

$$\omega_e=2170.0\ cm^{-1}$$

$$\omega_e x_e=13.45\ cm^{-1}$$

The vibrational frequency is:

$$\nu_{osc}=c\omega_e=\left(3\times10^{10}\ cm/\sec\right)\left(2170.2\ cm^{-1}\right)$$

$$=6.51\times10^{13}/\sec$$

The S.H. force constant is:

$$k=4\pi^2\mu\nu_{osc}^2$$

$$=4(3.14)^2\left(\frac{6.85841}{6.0251\times10^{25}}\right)\left(6.51\times10^{13}\right)^2$$

$$=1.90\times10^6\ dyne/cm$$

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6. The fundamental mode of HCl occurs at a $2886cm^{-1}$, predict the frequency of the corresponding mode of DCl.

Soln. The difference in frequency arises due to difference in mass of the isotopic molecules, we have

$$\nu_{osc}=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k is same for both the molecules as it is determined by electronic motion. If ω^i stands for the heavier isotope, then

$$\frac{\omega^i}{\omega}=\frac{\nu_{osc}^i}{\nu_{osc}}=\sqrt{\frac{\mu}{\mu^i}}=\rho\ (say)$$

$$\omega^i=\rho\omega$$

So that $\rho=\sqrt{\frac{\mu_{HCl}}{\mu_{DCl}}}=\sqrt{\frac{(1\times35)/(1+35)}{(2\times35)/(2+35)}}=\sqrt{\frac{35}{36}\times\frac{37}{70}}=\sqrt{\frac{37}{72}}=0.7168$

Treating the molecule as a harmonic oscillater the fundamental band occurs at $\omega\ cm^{-1}$, where ω is the vibrational constant. Here $\omega = 2886\ cm^{-1}$. For HCl.

$\therefore$ The fundamental band for DCl occurs at ω^i where,

$$\omega^i = \rho\omega = 0.7168 \times 2886\ cm^{-1} = 2069\ cm^{-1}$$

7. If the fundamental band H^1Cl^{35} lies at 3.46μ. Calculate the wavelength of the corresponding of H^2Cl^{37}.

Soln. If i stands for the heavier isotope, then

$$\frac{\omega^i}{\omega} = \sqrt{\frac{\mu}{\mu_i}} = \rho \qquad \ldots (i)$$

or, $\omega^i = \rho.\omega$

In terms of wavelength, we write

$$\lambda^i = \frac{1}{\rho}\lambda \qquad \ldots (ii)$$

where, $\rho = \sqrt{\frac{(1\times35)/(1+35)}{(2\times37)/(2+37)}} = \sqrt{\frac{35}{36}\times\frac{39}{74}} = 0.7158$

$\lambda = 3.46$ microns

Thus, equation (ii) $\Rightarrow \lambda^i = \frac{3.46 \text{ microns}}{0.7158} = 4.83$ microns

8. The $2886\ cm^{-1}$ fundamental band of the HCl can be shown to fit in the empirical equation.

$\nu(cm^{-1}) = 2885.90 + 20.577m - 0.3034m^2$. Calculate the value of B_e, B_0, & B_1. Given $\alpha_e = 0.3019\ cm^{-1}$

Soln. The general equation for the rotational lines to a band is:

$$\nu = \nu_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

Comparing it with the given equation for the fundamental ($v'' = 0, v' = 1$), band, we have

$$B_1 + B_0 = 20.577\ cm^{-1}$$

$$B_1 - B_0 = -0.3034\ cm^{-1}$$

Solving, we get

$$B_1 = 10.1368\ cm^{-1}$$

and $$B_0 = 10.4402\ cm^{-1}$$

We know the rotational constant corresponding to the vibrational state v is given by

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right)cm^{-1}$$

For the $v = 0$ state, we would have

$$B_0 = B_e - \frac{1}{2}\alpha_e$$

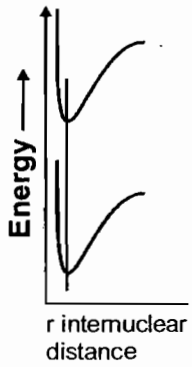
$$B_e = B_0 + \frac{1}{2}\alpha_e = 10.4402 + \frac{1}{2}(0.3019)\ cm^{-1}$$

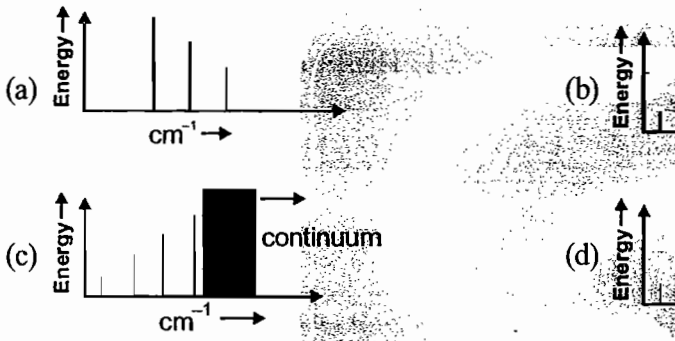
$$= 10.5909\ cm^{-1}$$

9. Which one of the following statement is ***INCORRECT*** in vibrational spectroscopy with anharmonicity?
(a) The selection rule for vibrational spectroscopy is $\Delta v = \pm 1, \pm 2, ...$ **[GATE 2008]**
(b) Anharmonicity leads to multiple absorption lines
(c) The intensities of hot band lines are stronger than the fundamental absorption.
(d) The frequencies of hot band lines are smaller than the fundamental absorption.

Soln. For vibrational spectroscopy with anharmonicity the selection rule is $\Delta v = \pm 1, \pm 2, \pm 3, ...$ The anharmonicity leads to multiple absorption lines. The intensity of hot band lines are stronger than the fundamental absorption is incorrect.
Hence, correct option is (c).

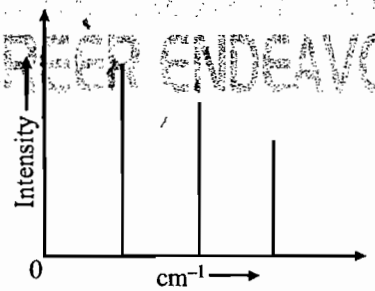
10. In a diatomic molecule, the internuclear separation of the ground and first excited electronic state are the same as shown in the figure. If the molecule is initially in the lowest vibrational state of the ground state, then the absorption spectrum will appear as





[GATE 2009]

Soln. For diatomic molecule, the internuclear separation of the ground and first excited state are the same. The absorption spectrum will appear for the transition from lowest vibrational state of the ground state will appear as shown in figure :



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Hence, correct option is (a).

11. The spectrum of radiation emitted by a black body at a temperature 1000 K peaks in the **[GATE-2010]**
(a) visible range of frequencies (b) infrared range of frequencies
(c) ultraviolet range of frequencies (d) microwave range of frequencies

Soln. For 1000 K, the energy $= k_B T = 1.38 \times 10^{-23} \times 1000 = 1.38 \times 10^{-20}$ joule

$$\text{Now, } \frac{hc}{\lambda} = 1.38 \times 10^{-20} \Rightarrow \lambda = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{1.38 \times 10^{-20}} = 1.43 \times 10^{-5} \text{ Hz.}$$

$\Rightarrow \lambda = 14.3\ \mu m$. i.e., wavelength in infrared region.
Hence, correct option is (b).

12. All vibrations producing a change in the electronic dipole moment of a molecule yield **[GATE-2004]**
(a) Raman spectra (b) Infrared spectra (c) Ultra-violet spectra (d) X-ray spectra

Soln. Infrared spectra will be observed by a change in the electric dipole moment of a molecule.
Hence, correct option is (b).

13. For a diatomic molecule with the vibrational quantum number n and rotational quantum number J, the vibrational level spacing $\Delta E_n = E_n - E_{n-1}$ and the rotational level spacing $\Delta E_j = E_j - E_{j-1}$ are approximately,

(a) ΔE_n = constant, ΔE_j = constant (b) ΔE_n = constant, $\Delta E_j \propto j$ **[GATE - 2005]**

(c) $\Delta E_n \propto n$, $\Delta E_j \propto j$ (d) $\Delta E_n \propto n$, $\Delta E_j \propto j^2$

Soln. The allowed energy for a harmonic oscillator is given by $E_n = \left(n + \frac{1}{2}\right) h\nu_{osc.}$, where n = 0, 1, 2, 3, ... is known as vibrational quantum number and in terms of wave number;

$\bar{\nu} = \frac{E_n}{hc} = \left(n + \frac{1}{2}\right)\frac{\nu_{osc.}}{c} = \left(n + \frac{1}{2}\right)\omega$, where ω is vibrational constant.

The selection rule of the vibrational transition gives : $\Delta n = \pm 1$. Thus, we get for n = D to n = 1 transition

$\Delta\bar{\nu} = \left(1 + \frac{1}{2}\right)\omega - \left(0 + \frac{1}{2}\right)\omega \Rightarrow \Delta\bar{\nu} = \omega$, which is independent of n. For rotational spectra, the energy difference in two levels j and (j – 1) is given by

$\Delta E_j = E_j - E_{j-1} = B\,hc\,(j)\,(j-1) - B\,hc\,(j-1)\,(j-2)$

$= B\,hc\left[j^2 - j - j^2 + 3j - 2\right] = B\,hc\left[j - 1\right]$, where j = 1, 2, 3, 4,....

Therefore, ΔE_j depends on j.
Hence, correct option is (b).

14. The typical wavelengths emitted by diatomic molecules in purely vibrational and purely rotational transition are respectively in the region of **[GATE - 2005]**
(a) infrared and visible (b) visible and infrared
(c) infrared and microwave (d) microwave and infrared

Soln. The typical wavelengths emitted by diatomic molecules in purely transitions lie in infrared region $(1\,\mu m - 10^2\,\mu m)$.
In purely rotational transitions, the typical wavelength lie in microwave region $(10^3\,\mu m - 10^4\,\mu m)$.
Hence, correct option is (c).

15. Two homonuclear diatomic molecules produce different rotational spectra, even though the atoms are known to have identical chemical properties. This leads to the conclusion that the atoms must be **[TIFR - 2016]**
(a) isotope, i.e., with the same atomic number
(b) isobar, i.e., with the same atomic weight
(c) isotones, i.e., with the same neutron number
(d) isomers, i.e., with the same atomic number and weight

Soln. Since, homonuclear diatomic molecules have atoms which have identical chemical properties. Thus, the atoms will have same place in periodic table. Hence, the atoms will be isotopes. Thus, the molecules give different rotational spectra.
Hence, correct option is (a).

16. The equilibrium vibration frequency for an oscillator observed at $2990 cm^{-1}$. The ratio of the frequencies corresponding to the first and the fundamental spectral lines is 1.96. Considering the oscillator to be anharmonic, the anharmonicity constant is

(a) 0.005 (b) 0.02 (c) 0.05 (d) 0.1

Soln. The equilibrium frequency $= 2990\, cm^{-1}$

For fundamental spactral line $\bar{\nu}_{0\to1} = \bar{w}_e(1-2x_e)cm^{-1}$

For first overtone, $\bar{\nu}_{0\to2} = 2\bar{w}_e(1-3x_e)cm^{-1}$

Now, according to question

$$\frac{\bar{\nu}_{0\to2}}{\bar{\nu}_{0\to1}} = \frac{2\bar{w}_e(1-3x_e)}{\bar{w}_e(1-2x_e)} = 1.96$$

$$\Rightarrow \quad \frac{2(1-3xle)}{(1-2x_e)} = 1.96$$

$$\Rightarrow \quad 2-6x_e = 1.96-3.92x_e$$

$$\Rightarrow \quad 2.08x_e = 0.04$$

$$\Rightarrow \quad x_e = 0.01923$$

$$\Rightarrow \quad \boxed{x_e = 0.02}$$

Thus, the anharmonicity constant is 0.02.

Hence, correct option is (b)

17. The spacing between vibrational energy levels in CO molecule is found to be $8.44\times10^{-1} eV$. Given that the reduced mass of CO is $1.14\times10^{-26} kg$, Planck's constant is 6.626×10^{-34} J-s and $1\text{ eV} = 1.6\times10^{-19}$ Joule. The force constant of the bond in CO molecule is

(a) 1.87 N/m (b) 18.7 N/m (c) 187 N/m (d) 1870 N/m

Soln. Difference between vibrational energy levels $= 8.44\times10^{-2} eV$

$= 8.42\times10^{-2}\times1.6\times10^{-19} J$

$= 13.472\times10^{-21}$ Joule

Reduced mass of CO molecule is $1.14\times10^{-26} kg$

Now, the relation between the force constant (k), reduced mass and frequency is given by

$$\nu_{osc.} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

For the CO molcule, the difference in two energy levels $= h\nu_{osc} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$

$$\Rightarrow \quad 13.472\times10^{-21} = \frac{6.626\times10^{-34}}{2\times3.14}\times\sqrt{\frac{k}{1.14\times10^{-26}}}$$

$$\Rightarrow \quad \sqrt{k} = \frac{2\times3.14\times13.472\times10^{-21}\times1.07\times10^{-13}}{6.626\times10^{-34}}$$

$$\Rightarrow \quad \sqrt{k} = 13.66231 \quad \Rightarrow \quad k = (13.66231)^2$$

$$k = 186.65$$

$$\Rightarrow \quad k = 187 \text{ N/m}$$

Hence, correct option is (c)

Chapter 8

Raman Spectra and Electronic Spectra

RAMAN EFFECT

Discovered by C.V. Raman in 1928 and won nobel prize in 1930.

Nature of Raman Spectran: Molecular spectra

Wave number of Rayleigh (excitting line or incident monochromatic light)

$$= \boxed{\nu_0 = \frac{1}{\lambda_0}} cm^{-1}$$

Wave number of stokes Raman line $= (\nu_0 - \Delta\nu) cm^{-1}$ and wave number of antistokes Raman line

$= (\nu_0 + \Delta\nu) cm^{-1}$

$\Delta\nu$ is fixed for a susbtance.

Intensity of Rayleigh line > Intensity of stokes line > Intensity of anti-stokes Raman line:

The change in the energy of the molecule is eitehr of vibrational energy or rotational energy. Therefore, Raman spectra is of two kind.

(i) Vibrational Raman spectrum

(ii) Pure rotational Raman spectrum

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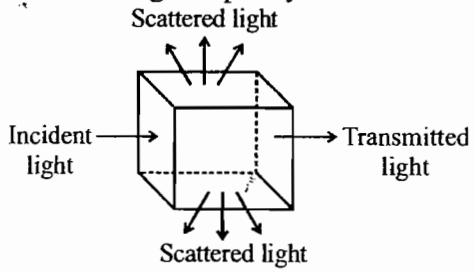
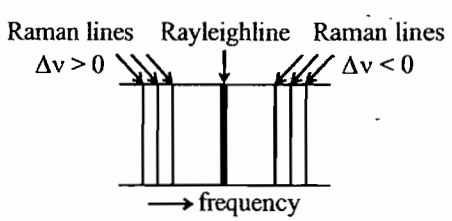
Raman Effect :

If a beam of monochromatic light is passed through the substance, nearly all of it is transmitted and a very small fraction of it is scattered in all directions. If the scattered light in a direction perpendicular to the incident beam is spectrographed, it is found not only to contain a line corresponding to the frequency of incident light, but also a pattern of relatively, weak lines on the low frequency side of the incident light and a similar pattern of still more weak lines on the high frequency side.





The line at the incident frequency is known as "Rayleigh line". The other weak lines are called the Raman lines. The difference between the frequencies of the Rayleigh line and a Raman line is known as the "Raman shift", and may be expressed as $\Delta\bar{\nu} = |\bar{\nu}_0 - \bar{\nu}_R|$, where the subscripts 0 and R stands for incident and Raman lines, respectively.

For a given substance, the Raman shift is found to be independent of the frequency of the incident radiation, i.e., it has the same value for the different frequency of the incident light. The difference is a characteristic of the substance and is found to be equal to its vibrational or rotational transition.

Classical theory of Raman effect :

The Raman spectroscopy is observed only when there occurs a periodic change in the polarizability of molecule due to its vibrational or rotational oscillation. From the classical point of view the above fact may be understood as follows.

In the presence of a static electric field, a molecule is polarized i.e., the positively charged nuclei and the negatively charged electronic cloud is attracted toward the respective oppositely charged pole of the electric field. Consequently, the molecule acquires an induced dipole moment which is given by $p_{ind} = \alpha E$, where α is the polarizability of the molecule. In the presence of a beam of radiation, each molecule will suffer electric field as $E = E_0 \sin(2\pi\nu t)$, where ν is the radiation frequency and thus the induced dipole also undergoes oscillations of frequency ν :

$$p = \alpha E = \alpha E_0 \sin(2\pi\nu t)$$

According to the electromagnetic theory, an oscillating dipole emits radiation of its own frequency. This explains the occurence of Rayleigh line in the light scattered by the substance.

If, in addition, the molecule undergoes some internal motion, such as vibration or rotation, which changes the polarizability periodically, then the oscillating dipole will have superimposed upon it the rotational or vibrational oscillation. We can write polarizability then as

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial \xi}\right) \xi_0 \sin(2\pi\nu_i t)$$

where, $\frac{\partial \alpha}{\partial \xi}$ is the change in the polarizability with the displacement coordinate ξ, ν_i the frequency of internal motion, and α_0 is the polarizability in the equilibrium position ξ_0, when we superimpose this upon the periodic oscillation due to electric field, we get

$$p_{ind} = \left\{\alpha_0 + \left(\frac{\partial \alpha}{\partial \xi}\right) \xi_0 \sin(2\pi\nu_i t)\right\} E_0 \sin(2\pi\nu t)$$

$$= \alpha_0 E_0 \sin(2\pi\nu t) + \left(\frac{\partial \alpha}{\partial \xi}\right) \xi_0 E_0 \sin(2\pi\nu_i t) \sin(2\pi\nu t)$$

Since, $\sin A \sin B = \frac{1}{2}\{\cos(A-B) - \cos(A+B)\}$

So, $p_{ind} = \alpha_0 E_0 \sin 2\pi\nu t + \frac{1}{2}\left(\frac{\partial \alpha}{\partial \xi}\right) \xi_0 E_0 \cos\{2\pi(\nu - \nu_i)t\} - \frac{1}{2}\left(\frac{\partial \alpha}{\partial \xi}\right) \xi_0 E_0 \cos\{2\pi(\nu + \nu_i)t\}$

That is, induced dipole moment of the molecule not only oscillates with frequency ν, but also with frequencies $(\nu - \nu_i)$ and $(\nu_i + \nu)$. It is thus expected that besides the frequency ν, the oscillating dipole will also emit radiations of frequencies $(\nu - \nu_i)$ and $(\nu_i + \nu)$. These radiations appear as the Raman lines in the light scattered by the substance.

Note: If $\frac{\partial \alpha}{\partial \xi}$ is zero i.e., there occurs no change in the polarizability during the small displacement from the equilibrium position of the internal, then the induced dipole oscillates only at the frequency of the incident

radiation. In such a case, the molecule emits only Rayleigh line and hence Raman lines are not observed, i.e. the molecule is Raman inactive.

Thus, the essential crietrion for a molecule to be Raman active is that a molecular vibration or rotation must cause a change in the component of molecular polarizability.

Quantum theory of Raman effect :

The occurence of Raman scattering may be most easily _____ radiation of frequency ν as consisting of a stream of particles called photons having energy $h\nu$. Photons can be imagined to undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged. A detector placed to collect energy at right angles to an incident beam will thus receive photons of frequency ν. This gives rise to "Rayleigh scattering".

On the other hand, if the collision is inelastic, there can occur an exchange of energy between molecule and photon. This exchange of energy can be of two types.

- The molecule before the collision occupies a lower vibrational or rotational energy level and after the emission of the photon, it may be present in anyone of the higher energy levels as permitted by selection rule. In this case, the molecule gains energy equivalent to the energy difference between the two involved levels. This energy is provided by the photon and hence its energy is decreased and thus a Raman line on the low frequency side is observed. Such a Raman line is called a "Stoke's line".
- The molecule before the collision occupies one of the higher vibrational or rotational energy level and after the emission of the photon may be present in any one of the lower energy levels as permitted by the selection rule. In this case, the molecule loses an energy equivalent to the energy difference between the two involved levels. This, energy is gained by photon and hence its energy is increased and thus a Raman line on high frequency side is observed. Such a Raman line is called an "anti-Stoke's" line.

Stoke's line is generally more intense than anti-stokes line.

The Stoke's lines frequency is $\frac{hc\nu - \Delta E}{hc}$

The anti-stoke's lines frequency is $\frac{hc\nu + \Delta E}{hc}$

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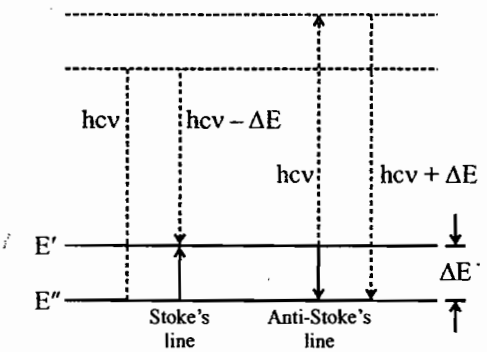
The wave number shift in each case being $\frac{\Delta E}{hc}$.



Pure rotational Raman spectra of diatomic molecules:

The rotational energy levels of linear molecules is $\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} (J = 0,1,2,3,...)$. But in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D, the centrifugal distortion constant.

So we take $\boxed{\varepsilon_J = BJ(J+1)}$ $(J = 0, 1, 2, ...)$

The selection rule for the pure rotational Raman spectra of diatomic molecules are $\Delta J = 0$ or ± 2 only.

The selection rule $\Delta J = 0$ gives rise to the Rayleigh scattering only. The selection rule $\Delta J = \pm 2$ gives rise to the Raman lines. The factor 2 is due to the fact that the polarizability ellipsoid rotates twice as fact that the polarizability ellipsoid rotates as fast as the rotation of the molecule.

The difference in wave number between two levels is $\Delta\varepsilon = BJ'(J'+1) - BJ''(J''+1)$

For the selection rule, $\Delta J = J' - J'' = +2$, we have $\Delta\varepsilon = \varepsilon_{J'=J''+2} - \varepsilon_{J''}$

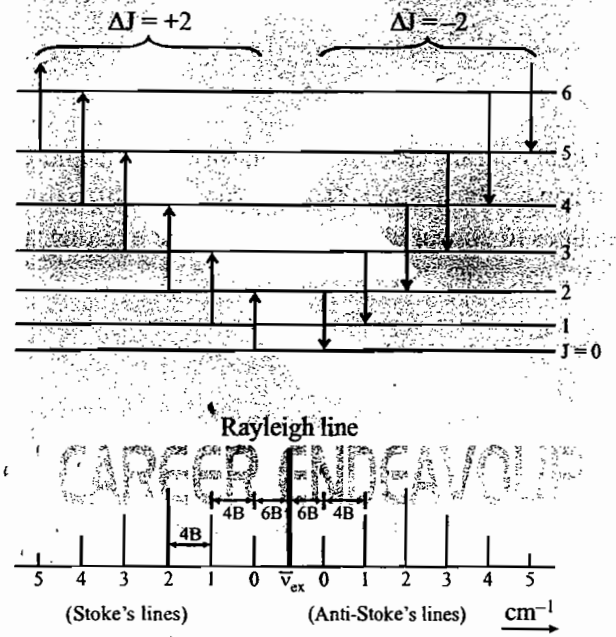
$\boxed{\Delta\varepsilon = B(4J''+6)}$ $J'' = 0, 1, 2, ...$

Similarly for the selection rule $\Delta J = J' - J'' = -2$, we have

$\Delta\varepsilon = \varepsilon_{J'=J'} - \varepsilon_{J''=J'-2} = -B(4J'+6)$ $J' = 0, 1, 2, ...$

Thus Raman lines will appear at wave number given by expression $\bar{\nu} = \bar{\nu}_{ex} \pm B(4J+6)$.

Here the plus sign refers to anti-stokes lines and minus to stokes line and $\bar{\nu}_{ex}$ is the wavenumber of the exciting radiation (i.e. Rayleigh line). The expected pure rotation Raman spectrum is shown in figure below.



The first stokes and anti-stokes line will lie at a separation of 68 from the Rayleigh line. The remaining lines will lie at a constant spacing of 48.

Each transition is labelled according to its lower J value and the relative intensities of the lines are indicated assuming that the population of the various energy levels varies according to the $\frac{N_J}{N_0} = (2J+1)\, e^{-(E_J - E_0)/kT}$.

Here we must note that stokes and anti-stokes lines have comparable intensity because many rotational levels are populated and hence downward transitions are approximately as likely as upwards ones.

It should be mentioned that, if the molecule has a center of symmetry (as, for example do O_2, H_2, CO_2) then the effects of nuclear spin will be observed in the Raman as in the infrared. Thus for O_2 and CO_2 (since the spin of oxygen is zero) every alternates rotational level is absent; for example, in case of O_2, every level with even J values is missing, and thus every transition labelled $J = 0, 2, 4, ...$ in above figure is also completely missing from the spectrum. In case of H_2, and other molecules composed of nuclei with non-zero spin, the spectral lines show an alternation of intensity.

The pure rotational Raman spectra provides the value B, and hence the moment of inertia and bond lengths for molecules. Homonuclear diatomic molecules do not exhibit pure vibrational or rotational spectra as they posses no dipole moment. But they do exhibit rotational Raman spectra and hence structural parameters which cannot be determined by pure rotational spectra can be determined from the Raman spectra.

Vibrational Raman spectra

For every vibrational mode we can write an expression of the form :

$$\varepsilon = \bar{\omega}_e\left(v+\frac{1}{2}\right) - \bar{\omega}_e x_e\left(v+\frac{1}{2}\right)^2 \text{ cm}^{-1} \quad (v = 0, 1, 2, 3, ...)$$

where, $\bar{\omega}_e$ is the equilibrium vibrational frequency and x_e is the anharmonicity constant. Such an expression is perfectly general, whatever the shape of the molecule of the nature of the vibration.

The selection rules for the vibrational Raman spectra are the same as those for pure vibrational spectra i.e. $\Delta v = 0, \pm 1, \pm 2, \pm 3, ...$ decreases rapidly.

Particularizing, now to Raman active modes, we can apply selection rule to the energy level expression given above, so

$v = 0 \rightarrow v = 1$; $\Delta\varepsilon_{\text{fundamental}} = \bar{\omega}_e(1-2x_e)$ cm^{-1}

$v = 0 \rightarrow v = 2$; $\Delta\varepsilon_{\text{overtone}} = 2\bar{\omega}_e(1-3x_e)$ cm^{-1}

$v = 1 \rightarrow v = 2$; $\Delta\varepsilon_{\text{hot}} = \bar{\omega}_e(1-4x_e)$ cm^{-1}

Since the Raman scattered light is, in any case, of low intensity we can ignore completely all the weaker effects such as overtones and 'hot bands', and restrict our discussion merely to the fundamentals.

We would expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibration. So we can write

$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \Delta\varepsilon_{\text{fundamental}}$ cm^{-1}

$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \bar{\omega}_e(1-2x_e)$

where the minus sign represents the stokes line and the plus sign refers to the anti-stokes line. Since the latter refers to the transitions $v = 1 \rightarrow v = 0$, it is expected to be very weak as very few molecules exist in the $v = 1$ state at the room temperature. On increasing temperature the population of $v = 0$ state is decreased whereas that of $v = 1$ state is increased, it is thus expected that the intensity of stoke's line will decrease whereas that of anti-stoke's line will increase on increasing the temperature of the sample.

The vibrational Raman spectrum of a molecule is then basically simple. It will show a series of reasonably intense lines to the low frequency side of the exciting line with a much weaker, mirror image series on high frequency side. The separation of each line from the center of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule.

The vibrational Raman spectra of homonuclear diatomic molecules are of special interest because they yield force constant and rotational constant that are not available from infrared absorption spectroscopy.

Intensity of the anti-stoke's Raman line is much smaller than that of stoke's Raman line.

$$\frac{\text{Anti-stoke's intensity}}{\text{Stoke's intensity}} = e^{-\Delta\varepsilon_{\text{fundamental}} \cdot hc/kT}$$

where, $\Delta\varepsilon_{\text{fundamental}} = \bar{\omega}_e(1-2x_e)$ is the Raman shift in vibration.

Raman activity of vibrations :

If a molecule has little or no symmetry it is a very straightforward matter to decide whether its vibrational modes will be Raman active or inactive : infact, it is usually correct to assume that all its modes are Raman active. However, when the molecule has considerable symmetry it is not always easy to make the decision, since it is some what not clear, without detailed consideration, whether or not the polarisability changes during the vibration.

Vibration modes of H_2O :

(a) ν_1, symmetric stretching mode : Raman active

(b) ν_2, bending mode : Raman active

(c) ν_3, asymmetric stretching mode : Raman active

(i) Vibrational Raman spectrum:

The selection rule is

$\Delta v = 0, \pm 1$

$\Delta v = 0$ leads to Rayleigh line

$\Delta v = \pm 1$ leads to stokes and antistokes raman lines.

$$\therefore \quad \nu_v^{\text{Raman}} = \nu_0 \pm \left[G(v+1) - G(v) \right]$$

$$= \nu_0 \pm \left[\omega\left(v+\frac{3}{2}\right) - w\left(v+\frac{1}{2}\right) \right]$$

$\nu_v^{\text{Raman}} = \nu_0 + \pm\omega$ (positive sign for antistokes and negative sign for stokes Raman line)

$\therefore \quad \left|\Delta\nu_v^{\text{Raman}}\right| = \omega$ Vibrational Raman shift.

For anharmonic treatment $\left|\Delta\nu_v^{\text{Raman}}\right| = \left(\omega_e - 2\omega_e x_e\right)$

(ii) Rotational Raman spectrum selection rule are

$\Delta J = 0, \pm 2$

$\Delta J = 0$, For Rayleigh line.

$$\therefore \quad \nu_{rot.}^{\text{Raman}} = \nu_0 \pm \left[F(J+2) - F(J) \right] \;\&\; \Delta J = \pm 2 \text{ for stokes and antistokes line}$$

$$= \nu_0 \pm \left[B(J+2)(J+3) - BJ(J+1) \right] \qquad [\text{as } F(J) = B\,J(J+1)]$$

$$= \nu_0 \pm (4BJ + 6B)$$

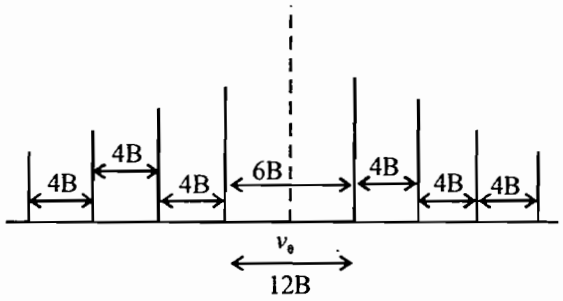
$$\boxed{\nu_{\text{rot.}}^{\text{Raman}} = \nu_0 \pm 4B\left(J+\frac{3}{2}\right)}$$

where, positive sign for antistokes Raman line and negative for stokes Raman lines.

and $\left|\Delta\nu_{rot.}^{Raman}\right| = 4B\left(J+\frac{3}{2}\right)$

where, $J = 0, 1, 2.....$

$\nu_{rot.}^{\text{Raman}} = \nu_0 \pm 6B, 10B, 14B, 18B.....$



Stokes line	**Antistokes line**
High intensity	Low intensity line
Stronglines	Weak line

Use:

1. To find Moment of inertia
2. To find bond length.
3. If Molequle symmetric = Raman spectra.

Raman ⇒ Active

Infrared ⇒ Inactive.

Raman Shift:

$$\Delta\nu = \frac{\Delta E}{hc}$$

Rule of Mutual Exclusion:

A further extremely important general rule has been established whose operation may be exemplified by carbon dioxide. we can summarize our conclusions about the Raman and infra-red activities of the fundamental vibrations of this molecule in Table and we see that, for this molecule, no vibration is simultaneously active in both Raman and infra-red. The corresponding general rule is:

Rule of mutual exclusion:

If a molecule has a centre of symmetry then Raman active vibrations are infra-red inactive, and vice versa. If there is no centre of symmetry then some (but not necessarily all) vibrations may be both Raman and infra-red active.

The converse of this rule is also true, i.e. the observance of Raman and infra-red spectra showing no common lines implies that the molecule has a centre of symmetry, but here caution is necessary since, as we have already seen, a vibration may be Raman active but too weak to be observed. However, if some vibrations are observed to give coincident Raman and infra-red absorptions it is certain that the molecule has no centre of symmetry. Thus extremely valuable structural information is obtainable by comparision of the Raman and infra-red spectra substance.

Mode of vibration of CO_2	Raman	Infra-red
ν_1 : symmetric stretch	Active	Inactive
ν_2 : bend	Inactive	Active
ν_3 : asymmetric stretch	Inactive	Active

i.e. Structure of CO_2 is O–C–O

Use of Raman effect.

Raman effect is used to determine the structure of diatomic molecules. By mutual exclusian principle "If the Infra red bands and Raman bands of a molecule not coincide the molecule will be linear and symmetric.".

Example: CO_2, CS_2 Raman bonds donot coincide with IR bands. Therefore, their structure is

O–C–O, S–C–S

Difference between IR spectra and Raman spectra:

IR spectra		Raman Spectra	
(i)	For showing IR spectra molecule must have permanent dipole moment	(i)	Molecule need not to have permanent dipole moment.
(ii)	Shown by hetronuclear molecules such as HCl, HBr, etc.	(ii)	Shown by homo as well as hetronuclear molecules.
(iii)	It is shown only when the energy of incident photon matches with the energy difference of two levels of molecule.	(iii)	It is not necessary here

ELECTRONIC SPECTRA: FRANCK-CONDON PRINCIPLE

Salient Features of Molecular Electronic spectra:

Among the molecular spectra, the electronic spectra are the most complex which appear in the visible and ultraviolet regions, and involve a change in all the three electronic, vibrational and rotational energies of the molecule. Such spectra are studied both in emission and absorption, and the (electronic) bands show a fine structure more complicated than in the vibrational-rotational bands. The tendency of head formation is much stronger, and the bands may be degraded either towards the red or toward the violet.

All diatomic molecules exhibit electronic spectra. Homonuclear molecules (H_2, N_2, O_2) which give neither rotational nor vibrational-rotational spectra because they do not have permanent dipole moments, give electronic spectra because the instantaneous dipole moment* changes during the redistribution of electronic charge which accompanies the electronic transition.

Dissociation Energy and Dissociation Products:

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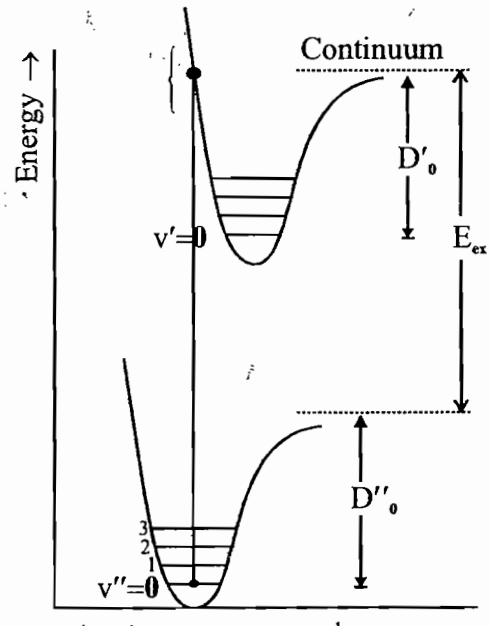
$\bar{\nu}_{\text{continuum limit}} = D''_0 + E_{ex}\ cm^{-1}$



D'_0 =Dissociation energy of molecule in upper electronic state.

D''_0 = energy of $(0,0) + D'_0 - E_{ex}\ cm^{-1}$.

Problem: The absorption spectra of O_2 shows vibrational structure which becomes a continuum at 56876 cm^{-1}. The upper electronic state dissociate into one ground state dissociate into one ground state atom and one excited state atom (the excitation energy of which, measured from the atomic spectrum is 15875 cm^{-1}). Estimate the dissociation energy of ground state of O_2 in kJ/mole.

Rotational Fine Structure of Electronic-Vibration Transitions:

To a very good approximation we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule as:

$$\varepsilon_{rot.} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1)\, cm^{-1} \quad (J = 0,1,2,.....)$$

$$\varepsilon_{total} = \varepsilon_{elec.} + \varepsilon_{vib.} + BJ(J+1)\, cm^{-1}$$

$$\Delta\varepsilon_{total} = \Delta\{\varepsilon_{elect.} + \varepsilon_{vib.}\} + \Delta\{BJ(J+1)\}\, cm^{-1}$$

$$\bar{\nu}_{spect.} = \bar{\nu}_{(\nu',\nu'')} + \Delta\{BJ(J+1)\}\ cm^{-1}$$

$$\Delta J = 0 \text{ or } \pm 1$$

$$J = 0 \not\longleftrightarrow J = 0$$

$$\nu_{spect.} = \bar{\nu}_{(\nu',\nu'')} + B'J'(J'+1) - B''(J''+1)\, cm^{-1}$$

1. **P-branch:** $\Delta J = -1,\ J'' = J'+1$

$$\Delta\varepsilon = \bar{\nu}_p = \bar{\nu}_{(\nu',\nu'')} - (B'+B'')(J'+1) + (B'-B'')(J'+1)^2\ cm^{-1}$$

where $J' = 0,1,2....$

2. **R-branch:** $\Delta J = +1,\ J' = J''+1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\nu}_{(\nu',\nu'')} + (B'+B'')(J''+1) + (B'-B'')(J''+1)^2\ cm^{-1}$$

Where $J'' = 0,1,2....$

These two equations can be combined into:

$$\bar{\nu}_{P,R} = \bar{\nu}_{(\nu',\nu'')} + (B'+B'')m + (B'-B'')m^2\ cm^{-1}$$

Where $m = \pm 1, \pm 2.....$

3. **Q-branch:** $\Delta J = 0 \quad \Rightarrow \quad J' = J''$ But $J' = J'' \neq 0$

$$\bar{\nu}_Q = \bar{\nu}_{(\nu',\nu'')} + (B'-B'')m + (B'-B'')m^2$$

The Fortrat Diagram: As

$$\bar{\nu}_{P,R} = \bar{\nu}_{(\nu',\nu'')} + (B'+B'')m + (B'-B'')m^2\ cm^{-1}$$

m = 0 for band origin.

The value of m at which the vertex of fortrat parabola lies is at

$$\frac{d\bar{\nu}_{P,R}}{dm} = 0$$

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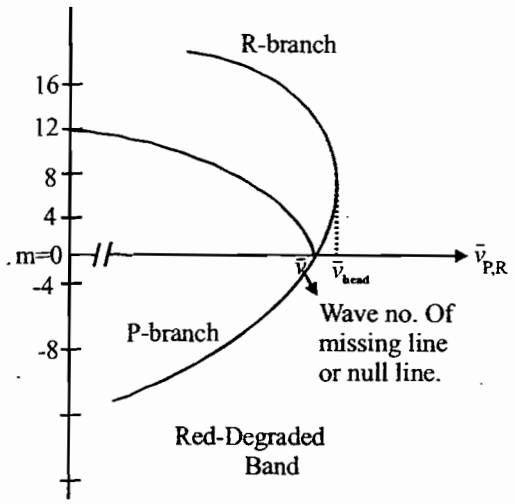

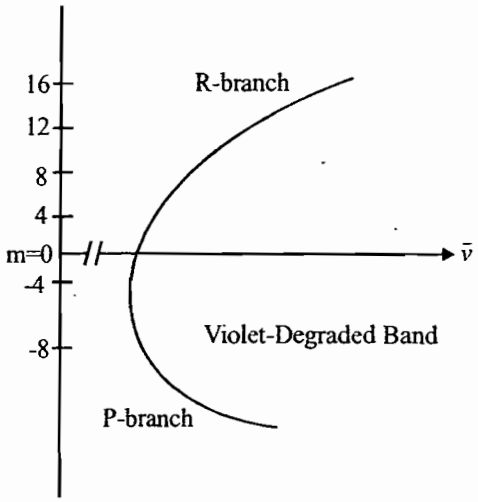

$$m_{vertex} = -\frac{(B'+B'')}{2(B'-B'')}$$

$$\therefore \quad \bar{\nu}_{head} = \bar{\nu} + (B'+B'')\left(\frac{(B'+B'')}{2(B'-B'')}\right) + (B'-B'')\left(\frac{B'+B''}{2(B'-B'')}\right)^2$$

$$\therefore \quad \bar{\nu}_{head} - \bar{\nu} = \frac{(B'+B'')}{4(B'-B'')}$$

If $\bar{\nu}_{head} - \bar{\nu} = +ive$ for a band degraded to the red and –ive for one degrated to the violet.

Problem: Rotational analysis of one band-system is given by $\bar{\nu} = 24762 + 1.25m - 2.1\,m^2 cm^{-1}$

Deduce the position of the band-head, the values of B' and B" and the degradation of the band.

Problem: The fine-structure lines of CN band at 3883.4Å can be represented by the following equation:

$\bar{\nu} = 25798 + 3.85\,m + 0.068\,m^2\ cm$

Calculate the separation between the null-line and the band-head and state the direction of degradation of the band.

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Franck Condon principle: Franck condon principle explain the variation of intensity among the bands of electronic band-system. The basic points of the Franck condon principle are:

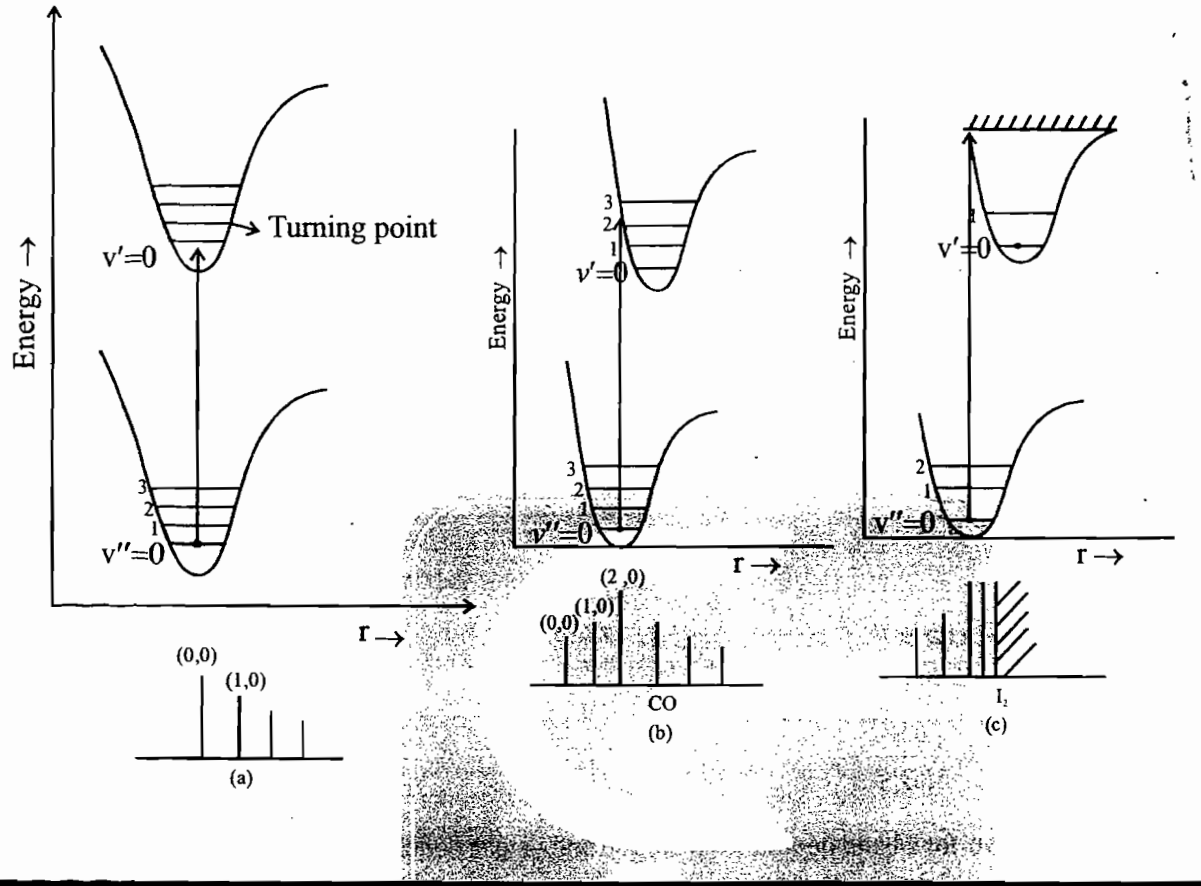
1. An electronic transition in a molecule takes place so rapidly compared to the vibrational motion of the nuclei that the instantaneous internuclear distance and the velocity of the nuclei can be considered remaining unchanged during the electronic transition.

   This means that in diagrams showing the potential energy curves of the two electronic states, the transitions must be represented by "Vertical lines".

2. The most probable (most intense) vibrational transitions are those in which one of the two turning points of a vibrational level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of a level of the other electronic state, except in case of v= 0 levels for which the mid-point rather than the turning point must be substituted.

Explanation of intensity distribution in absorption bands from Franck-condon principle:

Using the above two points the absorption transitions between two electronic states are shown in figure below.



SOLVED PROBLEMS

1. The number of fundamental vibrational modes of CO_2 molecule is :
   (a) Four: 2 are Raman active and 2 are infrared active
   (b) Four: 1 is Raman active and 3 are infrared active
   (c) Three: 1 is Raman active and 2 are infrared active
   (d) Three: 2 are Raman active and 1 is infrared active **[GATE-2007]**

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Soln. The number of fundamental vibrational modes of CO_2 molecule is three. Out of these, two are infrared active and one is Raman active.

2. A pure rotational Raman spectrum of a linear diatomic molecule is recorded using electromagnetic radiation of frequency u_e. The frequency of two consecutive stokes lines are : **[GATE 2008]**

   (a) $\upsilon_e - 10B, \upsilon_e - 14B$ (b) $\upsilon_e - 2B, \upsilon_e - 4B$

   (c) $\upsilon_e + 10B, \upsilon_e + 14B$ (d) $\upsilon_e + 2B, \upsilon_e + 4B$

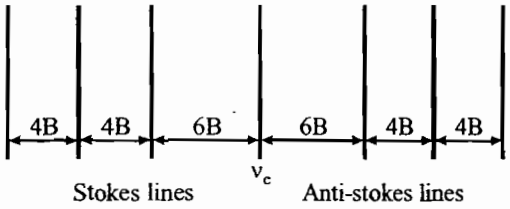
Soln. For Raman spectrum of a linear diatomic molecule, the frequency of two consecutive stokes lines are $\nu_e - 10B$ and $\nu_e - 14B$.

Hence, correct option is (a).

3. The separation between the first stokes and corresponding anti-stokes lines of the rotational Raman spectrum in terms of the rotational constant, B is : **[GATE 2009]**

   (a) 2B (b) 4B (c) 6B (d) 12B

Soln.



The separation between the first stokes and corresponding anti-stokes lines of the rotational Raman spectrum in terms of the rotational constant is 12B.

Hence, correct option is (d).

4. The far infrared rotational absorption spectrum of a diatomic molecule shows equivalent lines with spacing 20 cm^{-1}. The position of the first stokes line in the rotational Raman spectrum of this molecule is

(a) 20 cm^{-1} (b) 40 cm^{-1} (c) 60 cm^{-1} (d) 120 cm^{-1} **[GATE-2011]**

Soln. The line spacing in the infrared rotational absorption spectrum (2B) = 20 cm^{-1} $\Rightarrow$ B = 10 cm^{-1}

Since, the distance of first stokes lines from Rayleigh line is 6B.

Therefore, the position of first stoke line in the rotational Raman spectrum = $6 \times 10\ cm^{-1} = 60\ cm^{-1}$.

Hence, correct option is (c).

5. The excitation wavelength of laser in a Raman effect experiment is 546 *nm*. If the Stokes line is observed at 552 *nm*, then the wave number of the anti-Stokes line (in cm^{-1}) is _____

[GATE 2015]

Sol. The wave number of anti-stokes line is given by

$$\nu_{antistokes} - \nu_{Raman} = \nu_{Raman} - \nu_{stokes}$$

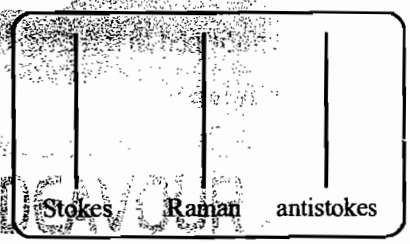
$$\Rightarrow \nu_{antistokes} = 2\nu_{Raman} - \nu_{stokes}$$

$$= 2 \times \frac{1}{(546\times10^{-7})} - \frac{1}{(552\times10^{-7})}$$

$$= 0.003663\times10^{7} - 0.0018116\times10^{7}$$

$$= 36630 - 18116 \text{ per cm}$$

$$= 18514 \text{ per cm}$$



Hence correct answer is 18514 per cm.

6. Match the phrases in Group I and Group II and identify the correct option. **[GATE 2015]**

Group I	**Group II**
(P) Electron spin resonance (ESR)	(i) radio frequency
(Q) Nuclear magnetic resonance (NMR)	(ii) visible range frequency
(R) Transition between vibrational states of a molecule	(iii) microwave frequency
(S) Electronic transition	(iv) far-infrared range

(a) (P-i), (Q-ii), (R-iii), (S-iv) (b) (P-ii), (Q-i), (R-iv), (S-iii)

(c) (P-iii), (Q-iv), (R-i), (S-ii) (d) (P-iii), (Q-i), (R-iv), (S-ii)

Soln. P. ESR (electron spin resonance) is used in GHz [8 – 10 GHz] frequency range. Thus, it is microwave range.

Q. NMR (nuclear magnetic resonance) is used in MHz [100 – 1000] frequency range. Thus, it is in radiofrequency range.

R. Transition between vibrational states of a molecule lies in frequency range (10^{12} to 10^{14} Hz). Thus, it lies in far-infrared range.

S. Electronic transition lies in frequency range 10^{14} to 10^{15} Hz. Thus, it lies in visible range.

Hence, correct option is (c).

7. Light of wavelength 1.5 μm incident on a material with a characteristic Raman frequency of 2×10^{12} Hz results in a stokes-shifted line of wavelength. **[GATE-2004]**
[Given : $C = 3 \times 10^8$ m/sec].
(a) 1.47 μm (b) 1.57 μm (c) 1.67 μm (d) 1.77 μm

Soln. The frequency of the light of wavelength 1.5 μm incident on material is

$$\nu = \frac{c}{\lambda} = \frac{3\times10^8}{1.5\times10^{-6}} = 2\times10^{14}\ \text{Hz}$$

This will be the exciting line i.e. Rayleigh line and the frequency of Raman line is $\nu_{Raman} = 20\times10^{12}$ Hz
Therefore, the Raman shift

$$\Delta\nu = \nu - \nu_{Raman} = 2\times10^{14} - 20\times10^{12}\ \text{Hz}$$
$$= 180\times10^{12}\ \text{Hz}$$

In terms of wavelength, the Raman shift is given by

$$\Delta\lambda = \frac{3\times10^8}{180\times10^{12}} = 1.67\times10^{-6}\ \text{m}$$
$$= 1.67\ \mu\text{m}$$

Hence, correct option is (c).

8. In a Raman scattering experiment, light of frequency ν from a laser is scattered by diatomic molecules having the moment of inertia I. The typical Raman shifted frequency depends on **[GATE - 2005]**
(a) ν and I (b) only ν (c) only I (d) neither ν nor I

Soln. The rotational Raman shift is given by $\left|\Delta\nu\right|^{\gamma}_{Raman} = 4B\left|J+\frac{3}{2}\right| = 6B, 10B, 14B, \ldots$ where $J = 0, 1, 2, \ldots$ and $B = \frac{h}{8\pi^2 Ic}$. Thus, it is confirmed that the typical Raman shifted frequency depends only on I.
Hence, correct option is (c).

9. A vibrational electronic spectrum of homonuclear binary molecules, involving electronic ground state ε'' and excited ε', exhibits a continuum at $\bar{\nu}$ cm^{-1}. If the total energy of dissociated atoms in the excited state exceeds the total energy of the dissociated atoms in the ground state by $E_{ex.}$ cm^{-1}, the dissociation energy of the molecule in the ground state is **[GATE - 2006]**

(a) $\frac{(\bar{\nu}+E_{ex.})}{2}$ (b) $\frac{(\bar{\nu}-E_{ex.})}{2}$ (c) $(\bar{\nu}-E_{ex.})$ (d) $\sqrt{(\bar{\nu}^2-E_{ex.}^2)}$

Soln. The dissociation energy of the homonuclear molecule will be $(\bar{\nu}-E_{ex.})$.
Hence, correct option is (c).

10. The NMR spectrum of ethanol (CH_3CH_2OH) comprises of three bunches of spectral lines. The number of spectral lines in the bunch corresponding to CH_2 is **[GATE - 2006]**
(a) 1 (b) 2 (c) 3 (d) 4

Soln. The number of spectral lines in the bunch corresponding to CH_2 is 4.
Hence, correct option is (d).

11. Consider the following statements about molecular spectra : **[GATE - 2003]**

P : CH_4 does not give pure rotational Raman lines.

Q : SF_6 could be studied by rotational Raman spectroscopy.

R : N_2 shows infrared absorption spectrum.

S : CH_3CH_3 shows vibrational Raman and infrared absorption lines.

T : H_2O_2 shows pure rotational spectrum.

Choose the right combination of correct statements :

(a) P and Q (b) P, R and T (c) P, S and T (d) Q and R.

Soln. Only options P, S and T are correct.

Hence, correct option is (c).

12. The molecule $^{17}O_2$ is **[GATE 2016]**

(a) Raman active but not NMR (nuclear magnetic resonance) active

(b) Infrared active and Raman active but not NMR active

(c) Raman active and NMR active

(d) Only NMR active

Soln. $^{17}O_2$ is a homonuclear molecules, while necessarily have zero dipole moment, fail to interact with radiation. These molecules gives Raman spectra.

Also, the $^{17}O_2$ molecule has non zero (finite) nuclear spin and quadrupole moment. Thus, it will also show NMR spectra.

Hence correct option is (c)

13. Match the following: **[GATE-2007]**

P: Franck-Hertz experiment	1. Electronic excitation of molecules
Q: Hartree-Fock method	2. Wave function of atom
R: Stern-Gerlach experiment	3. Spin angular momentum of atoms
S: Franck-Condon principle	4. Energy levels in atoms

(a)	(b)	(c)	(d)
P-4	P-1	P-3	P-4
Q-2	Q-4	Q-2	Q-1
R-3	R-3	R-4	R-3
S-1	S-2	S-1	S-2

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Soln. P : Frank-Hertz experiment was performed to identify to energy levels in atoms.

Q : Hartree-Fock method is used for the wave functions of atoms.

R : Stern-Gerlach experiment was performed to check the space quantisation of "spin angular momentum of atoms".

S : Frank-Condon principle was given for the electronic excitation of molecules.

Hence, correct option is (a).

Chapter 9

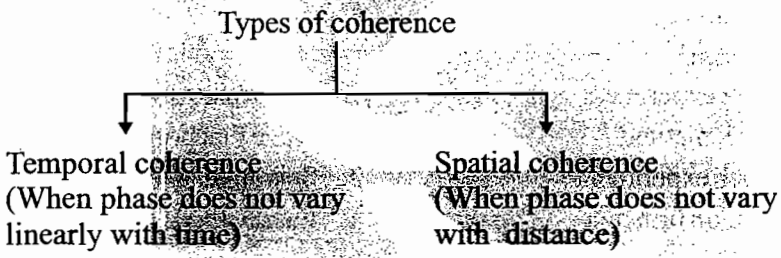
Laser Physics

TEMPORAL & SPATIAL COHERENCE

Coherence:

A wave which appears to be a pure sine wave for an infinitely long period of time, or in an infinitely extended space, is said to be a perfectly coherent wave. In such a wave there is a definite relationship between the phase of the wave at a given time and at a certain time later, or at a given point and at a certain distance away. No actual light source, however, emits a perfectly coherent wave. Light waves which are pure sine waves only for a limited period of time or in a limited space are partially coherent waves.

There are two different criteria of coherence; the criteria of time and the criteria of space. This gives rise to temporal coherence and spatial coherence.


Types of coherence
Temporal coherence
(When phase does not vary linearly with time)
Spatial coherence
(When phase does not vary with distance)

Coherence time Coherence length: The average time interval for which definite phase relationship exists is known as coherence time (τ) of the light beam. The distance (L) for which the field is sinusoidal is given by

$$L \doteq \tau c$$

where, c is speed of light, L is coherence length of the light beam.

Temporal Coherence as related with Monochromaticity of Spectral line:

If wavelength spread is $\Delta\lambda$ i.e. the light beam consist of all wavelength lying between λ and $\lambda + \Delta\lambda$, then the interference pattern produced by wavelengths λ and $\lambda + \frac{1}{2}\Delta\lambda$ would disppear, if $L = \frac{\lambda^2}{\Delta\lambda}$.

If $\Delta\lambda = 0$

$\Rightarrow$ L = infinite, τ = infinite

i.e. perfectly temporal coherence.

In terms of frequency;

$$\Delta\nu = \frac{c}{\lambda^2}\Delta\lambda \quad [\text{as } \nu = \frac{c}{\lambda}, \Delta\nu = \frac{c}{\lambda^2}\Delta\lambda,]$$

$$\Rightarrow \quad \Delta\nu = \frac{c}{L} = \frac{1}{\tau}$$

i.e. longer is the coherence time, the smaller is the frequency spread.

Spatial Coherence:

The spatial coherence is the phase relationship between the radiation fields at different points in space. Let us consider light waves emitting from a source S. Let A and B be two points lying on a line joining them with S. The phase relationship between the points A and B depends on the distance AB and on the temporal coherence of the beam. If

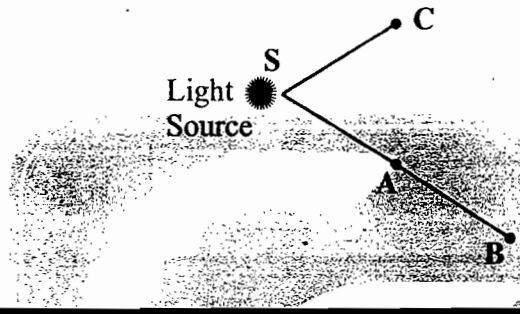
$AB << L$ (coherence length),

there will be a definite phase relationship between the points A and B, that is, there will be high coherence betwen the points A and B. On the other hand, if

$AB >> L$,

there will be no coherence between the points A and B.

Let us now consider points A and C which are equidistant from S. If the source S is a true point source, then the waves shall reach the points A and C in exactly the same phase, that is, the two points will have perfect (spatial) coherence. If, however, the source S is extended, the points A and C will no longer remain in coherence.



LASER

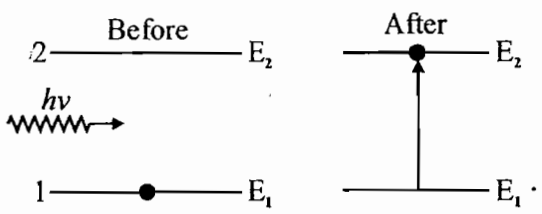
The word 'LASER' is an acronym for Light Amplification by Stimulated Emission of Radiation. It is a source which emits an intense, almost perfectly monochromatic, directional, and highly coherent baem of light. Its working depends on the phenomenon of "stimulated emission", first predicted by Einstein in 1916.

Interaction of Radiation with Matter: An atomic system is characterised by discrete energy states, and usually the atoms occupy the lowest energy state, known as the ground state. An atom in a lower energy state may be excited to a higher energy state through a number of processes, one process being absorption of electromagnetic radiation of proper frequency. On the other hand, an atom in an excited state can transit to a lower energy state through the emission of electromagnetic radiation. The emission may be spontaneous or stimulated, as predicted by Einstein. Let us consider these processes separately.

1. (Stimulated) Absorption of Radiation:

An atom, initially in a lower state 1, rises to a higher state 2 by absorbing a quantum of suitable radiation (photon) of frequency ν, given by

$\nu = \frac{E_2 - E_1}{h}$, where, E_1 and E_2 are the energies of the atom in the states 1 and 2 respectively.



(Stimulated Absorption)

Fig.

The probability per unit time per atom of absorbed emission depends on the energy density $u(\nu)$ and is given by

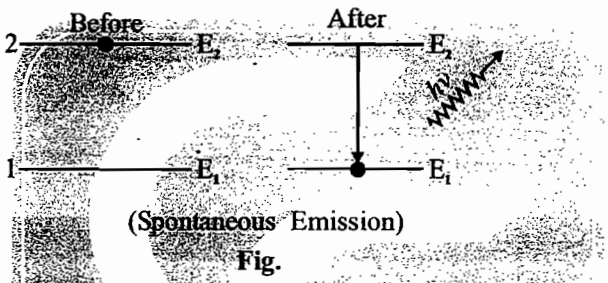
$$B_{12}\, u(\nu)$$

where, B_{12} is proportionality constant known as Einstein's 'B' coefficient of stimulated absorption. If N is the number of atoms/m^3 in such a group which take part in absorption (i.e. density of atoms) in lower energy state, then the rate at which stimulated absorption occurs is given by

$$\frac{\partial N}{\partial t} = -B_{12} u(\nu) N$$

2. Spontaneous emission:

An atom initially in the higher energy state 2 usually stay there for a short duration of 10^{-8} sec and decays to lower energy state 1, in its own accord, emitting a photon of freqency $\nu = \left(\frac{E_2 - E_1}{\lambda}\right)$. This is 'spontaneous' emission of radiation.



(Spontaneous Emission)

Fig.

The probability per unit time of an atom to decay spontaneously is independent of the incident radiation and is given by

A_{21} which is Einstein's coefficient of spontaneous emission.

If N is the number of atoms/m^3 at time t in a group, decay spontaneous in upper energy state, then the rate at which spontaneous emission occurs is given by

$$\frac{\partial N}{\partial t} = -A_{21} N$$

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$$\Rightarrow \quad \frac{\partial N}{N} = -A_{21} t$$

$$\Rightarrow \quad \ln N = -A_{21} + \ln C$$

At $\quad t = 0,\ u = N_0 \quad \Rightarrow \quad C = N_0$

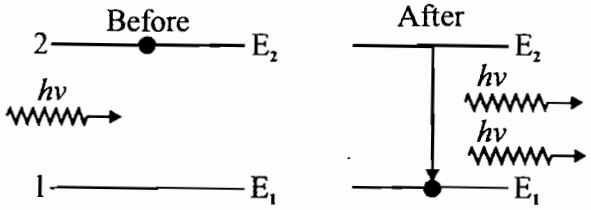
$$\Rightarrow \quad \ln \frac{N}{N_0} = -A_{21} t$$

$$\Rightarrow \quad N = N_0 e^{-A_{21}t} \text{ or } N = N_0 e^{-t/t_{sp}}$$

where, $t_{sp} = \frac{1}{A_{21}}$ =Average life time of an atom in emitted state before decaying spontaneously.

3. Stimulated Emission of Radiation: According to Einstein, an atom in an excited energy state, under the influence of the electromagnetic field of a photon of frequency ν incident upoin it, decays to a lower energy state, emitting an additional photon of same frequency ν. Thus, one incident and the other emitted, move on. This is 'stimulated' (or induced) emission of radiation. The direction of propagation, energy, phase and state of

polarisation of the emitted photon is exactly the same as that of the incident stimulating photon. In other words, the stimulated radiation is completely coherent with the stimulating radiation. As a result of this process, radiation passing through an assembly of atoms is amplified.



(Stimulated Emission)

Fig.

The probability per unit time of an atom to decay by stimulated emission depends upon the energy density of the incident radiation and is given by

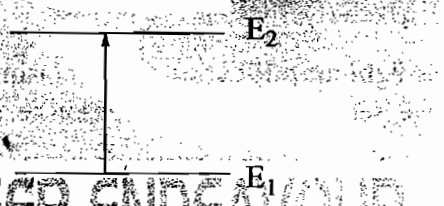
$B_{21}u(v)$ where, B_{21} is 'Einstein's 'B' coefficient of stimulated emission of radiation'.

In a group of such atoms, if the density of atoms in the emitted emitted state is N, the rate at which stimulated emission occurs is given by

$$\frac{\partial N}{\partial t} = -B_{21}u(v)N$$

Relation Between Einstein Coefficients:

If spectral energy density is u(v) at temperature T. The probability rate of occurrence of the absorption transition $1 \rightarrow 2$ would be proportional to N_1 and also to u(v). Thus, the number of absorption transitions per unit time per unit volume can be written as energy density $N_1 B_{12} u(v)$, where B_{12} is Einstein's absorption Coefficient.



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The probability rate of spontaneous emission $2 \rightarrow 1$ is determined only by the properties of the states 2 and 1, and is proportional to the number of atoms N_2 in the energy state 2. Thus, the number of spontaneous emission transitions per unit time per unit volume can be written as

$$N_2 A_{21}.$$

Again, the proportionality constant A_{21}, depends on the properties of energy staes 2 and 1, and is known as 'Einstein's 'A' coefficient of spontaneous emission of radiation'.

Finally, the probability rate of stimulated emission transition $2 \rightarrow 1$ is proportional to the energy density u(v) of the stimulating radiation. Thus, the number of stimulated emission transitions per unit time per unit volume can be written as

$$N_2 B_{21} u(v),$$

where, B_{21} is 'einstein's 'B' coefficient of stimulated emission of radiation'.

At thermal equilibrium, the number of upward transitions $1 \rightarrow 2$ should be equal to the number of downward transitions $2 \rightarrow 1$, that is,

$$N_1\left[B_{12}\, u(v)\right] = N_2\left[A_{12} + B_{21}u(v)\right]$$

$$\Rightarrow \quad \frac{N_1}{N_2} B_{12}\, u(\nu) = A_{21} + B_{21}\, u(\nu)$$

$$\Rightarrow \quad \left[\frac{N_1}{N_2} B_{12} - B_{21}\right] u(\nu) = A_{21}$$

$$\Rightarrow \quad u(\nu) = \frac{A_{21}}{\left(\frac{N_1}{N_2} B_{12} - B_{21}\right)} = \frac{A_{21}/B_{21}}{\left[\frac{N_1}{N_2}\left(\frac{B_{12}}{B_{21}}\right) - 1\right]}$$

$$\Rightarrow \quad u(\nu) = \frac{A_{21}/B_{21}}{\left(\frac{B_{12}}{B_{21}}\right)\left(\frac{N_1}{N_2}\right) - 1}$$

$$\Rightarrow \quad u(\nu) = \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}}\left(e^{h\nu/kT}\right) - 1} \quad \left(\text{where, } \frac{N_1}{N_2} = e^{h(E_2 - E_1)/kT} = e^{h\nu/kT}\right)$$

Using Planck radiation formula, $u(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\left(e^{h\nu/kT} - 1\right)}$

We get, $\frac{B_{12}}{B_{21}} = 1$ and $\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$

These are called as relation between Einstein Coefficient.

Necessary condition for light amplification (i.e. for lasing action):

The condition is to achieve (set up) population inversion i.e. to have more number of atoms in higher energy state (violation of Boltzmann's distribution law) i.e. to have $N_2 > N_1$ for stimulated emission.

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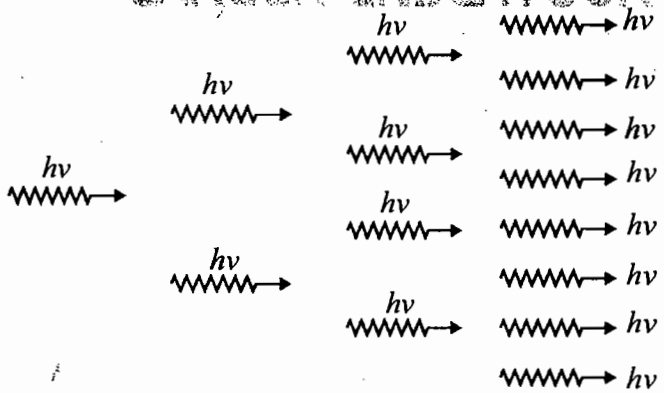


Fig.

Stimulated emission are further encouraged by increasing the radiation density u(v) of the stimulating radiation. This is achieved by enclosing the emitted radiation in a "cavity" between two parallel reflectors. The radiation repeatedly travels back and forth, and the photons passing through the atoms go on multiplying by repeated stimulated emission. Hence a strong coherent beam of light emerges from the system.

Achievement of population inversion: Pumping:

For any laser device to operate, the achievement of population inversion in the active medium is necessary. That is, a larger number of atoms of the medium should be excited to higher energy states. **The process by which atoms are raised from a lower to a higher energy state is called "pumping" of atoms.** The pumping process in lasers involves a number of energy levels with complex excitation processes. Different methods of atomic excitations are adopted in different types of lasers. Some of the methods are:

(i) Excitation by a strong source of light, say flash lamp or arc lamp (optical pumping),

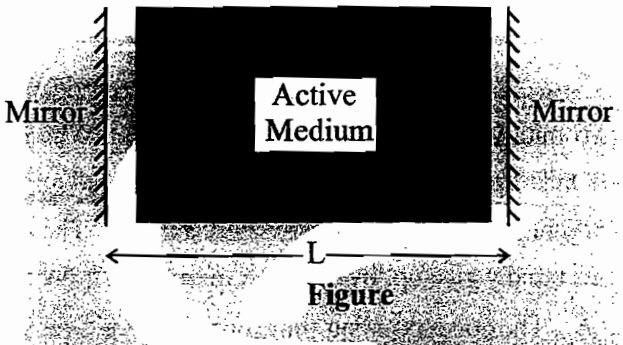
(ii) Exication by electron impact (electrical pumping),

(iii) Excitation by chemical reaction (Chemical pumping),

(iv) Excitation by supersonic gas expansion (gas-dynamic pumping), and so on.

Optical Resonator:

A medium with population inversion is capable of amplifying a light beam passing through it. However, if the medium is to act as an oscillator which can supply light energy and act as a source of light, a part of the output energy must be fed back into the medium.



Figure

Such a feedback can be achieved by placing the active medium between two mirrors facing each other (above Figure). The mirrors reflect most of the output energy back to the medium. Such a system formed by two mirrors represents a reasonant cavity, and is referred to as an optical resonantor. To obtain an output light beam, one of the mirrors is made partially reflecting.

Let us consider a wave which starts from one of the mirrors and travels towards the other. In passing through the active medium, the wave is amplified. If the second mirror is partially reflecting, then the wave is partially transmitted and the rest is reflected back towards the first mirror. In travelling to the first mirror, the wave is again amplified and returns to its starting position. Thus, in between the two mirrors, there are waves propagating along both directions. These wave interfere, and for a stable standing wave pattern to be formed in the cavity, the total phase change suffered by the wave in one complete round trip must be an integral multiple of 2π. Thus, if L is the length of the cavity, then

$$\frac{2\pi}{\lambda}(2L) = 2m\pi; \qquad m = 1, 2, 3..... \qquad ... (1)$$

where λ is the is the wavelength of the radiation in the medium enclosed by the cavity.

Now, $\lambda = c/\nu$, where ν is frequency of the radiation. Then, equation (1) gives

$$\nu = m\frac{c}{2L}$$

which gives the discrete frequencies of oscillation. Different values of m lead to different oscillation frequencies which constitute the longitudinal modes of the cavity. The frequency difference between adjacent longitudinal modes is:

$$\Delta\nu = \frac{c}{2L}$$

Types of Lasers:

1. The Ruby Laser - A Three-level System:

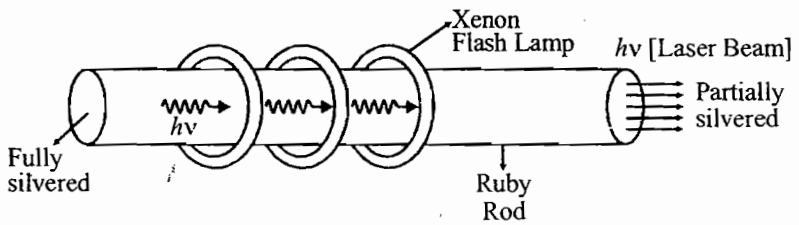
The ruby laser was the first laser developed in 1960. It is a solid-state laser. It consists of a pink ruby cylindrical rod whose ends are optically flat and parallel (Figure below). One end is fully silvered and the other is partially silvered. The two ends thus form a resonant cavity. The ruby rod is placed inside a coiled xenon flash lamp. The flash lamp is connected to a capacitor (not shown) which discharges a few thousand joules of energy in a few milliseconds, resulting in a power output of a few megawatts from the flash lamp.

Working: The ruby rod is a crystal of aluminium oxide (Al_2O_3) doped with 0.05% chromium oxide (Cr_2O_3), so that some of the Al^{+++} ions are replaced by Cr^{+++} ions. These "impurity" chromium ions give pink colour to the ruby and give rise to the laser action.

A simplified version of the energy-level diagram of chromium ion is shown in Figure (below). It consists of an upper short-lived energy level (rather energy band) E_3 above its ground-state energy level E_1, the energy difference $E_3 - E_1$ corresponding to a wavelength of ab out 5500 Å. There is an intermediate excited-state level E_2 which is metastable having a life-time of 3×10^{-3} s (about 10^5 times greater than the life-time of E_3 which is $\approx 10^{-8}$ s).

Normally, most of the chromium ions are in the ground state E_1. When a flash of light (which lasts only for about a millisecond) falls upon the ruby rod, the 5500 Å radiation photons are absorbed by the chromium ions which are "pumped" (raised) to the excited state E_3. The trasition 1 is the (optical) pumping transition. The excited ions rapidly give up, by collision, part of their energy to the crystal lattice and decay to the "metastable" state E_2. The corresponding transition 2 is thus a radiationless transition. since the state E_2 has a much longer life-time, the number of ions in this state goes on increasing while, due to pumping, the number in the ground state E_1 goes on decreasing. Thus, population inversion is established between the metastable (excited) state E_2 and the ground stae E_1.

when an (excited) ion passes spontaneously from the metastable state to the ground state (transition 3), if it emits a photon of wavelength 6943 Å this photon travels through the ruby rod and, if it is moving parallel to the axis of the crystal, is reflected back and forth by the silvered ends until it stimulates an excited ion and causes it to emit a fresh photon in phase with the stimulating photon. This "stimulated" transition 4 is the laser transition. (The photons emitted spontaneously which do not move axially escape through the sides of the crystal). The process is repeated again and again because the photons repeatedly move along the crystal, being reflected from its ends. The photons thus multiply. When the photon-beam becomes sufficiently intense, part of it emerges through the partially-silvered end of the crystal.



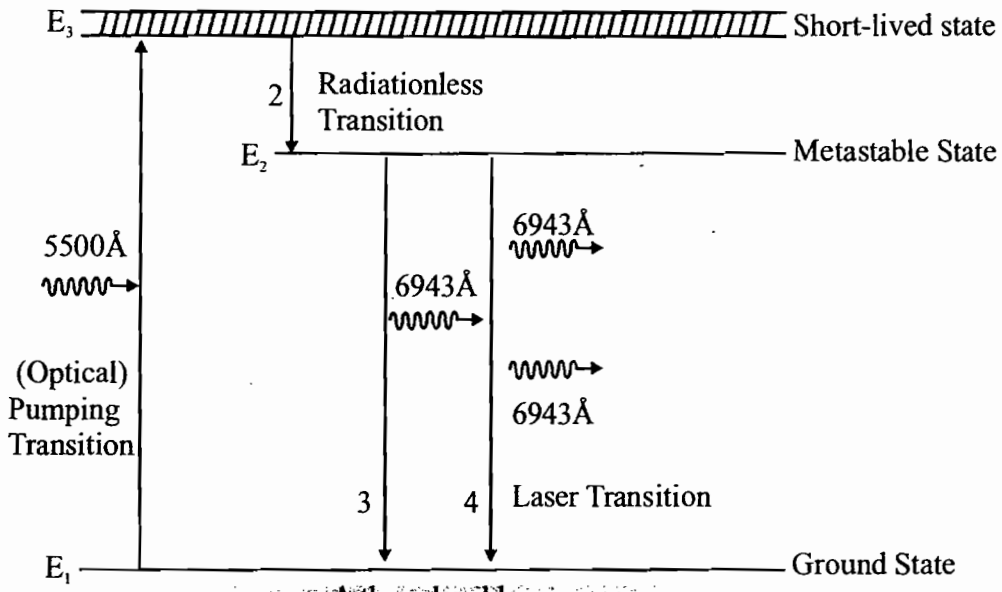
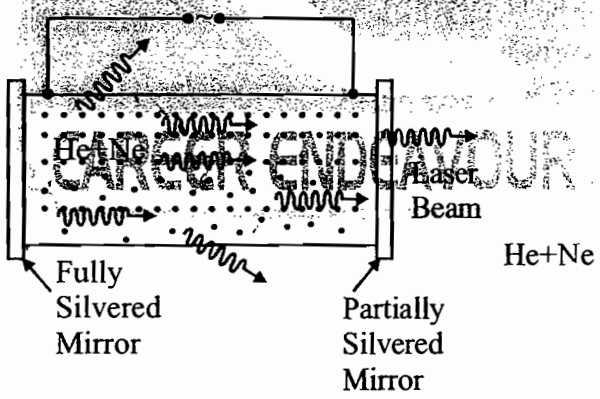


Figure: Energy level diagram of Ruby Laser

(ii) The Helium-Neon Laser:(Four level Laser):

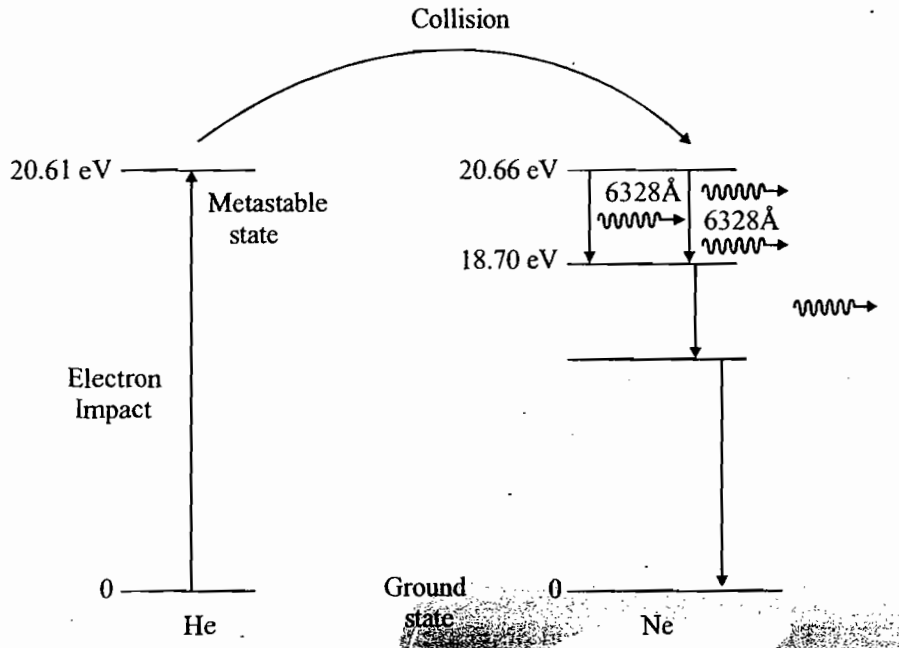
The Helium-Neon laser was the first gas laser to be operated successfully. It was fabricated by Javan in 1961. It is a four-level laser in which population inversion is achieved by electric discharge.

The Helium-neion laser consists of a long and narrow discharge tube filled with a mixture of He and Ne in a ratio of about 10:1 at a pressure of about 1 mm of mercury. The gas mixtrue (He+Ne) forms the lasing medium.



It is placed between a pair of optically plane and parallel mirrors which form a resonant cavity. One of the mirrors is fully silvered and the other is partially silvered. The spacing of mirrors is equal to an integral number of half-wavelengths of the laser light. An electric discharge may be produced in the gas-mixture by electrodes connected to a high-frequency electric source.

Working: When a discharge through the gas mixture, electrons are accelerated down the tube. These accelerated electrons collide with, and "pump" (excite) the He and Ne atoms to metastable states 20.61 eV and 20.66 eV respectively above their ground states (Figure below). Some of the excited He atoms transfer their energy to ground-state



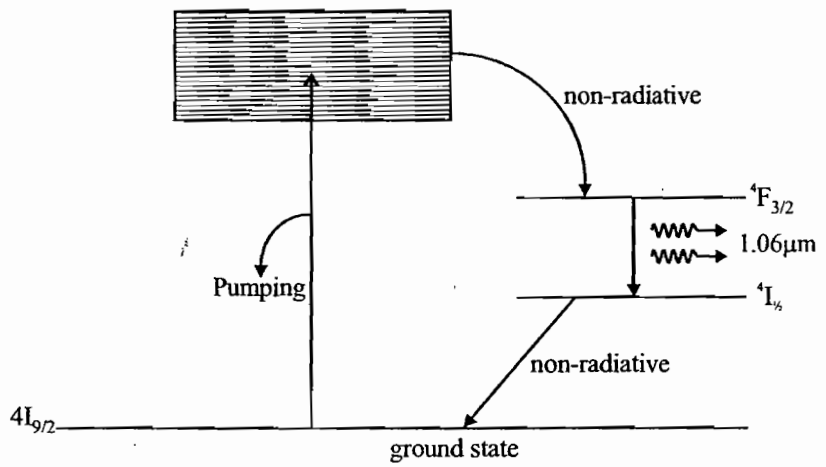
A four-level laser

Ne atoms by collision, with the 0.05 eV of addition energy being provided by the kinetic energy of atoms*. Thus, He atoms help in achieving a population inversion in the Ne atoms.

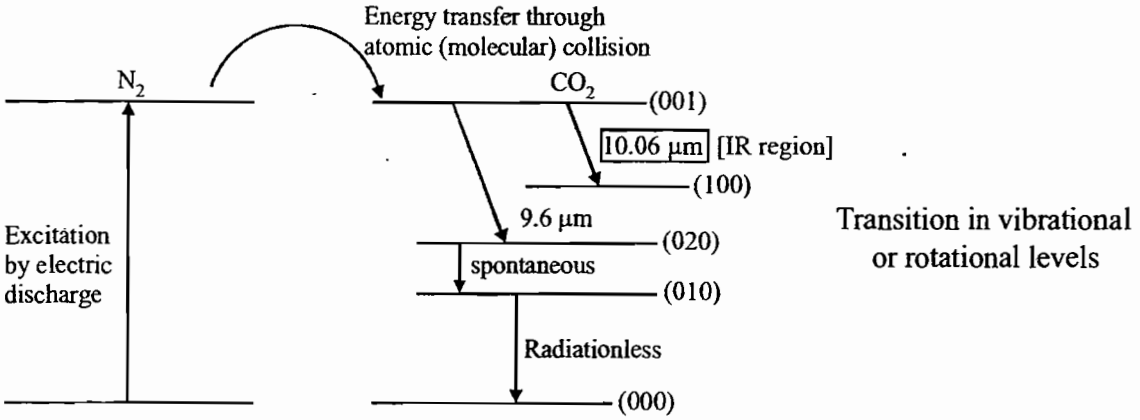
When an excited Ne atom passes spontaneously from the metastable state at 20.66 eV to be the state at 18.70 eV, it emits a 6328.-Å photon. This photon travels through the gas-mixture and if it is moving parallel to the axis of the tube, is reflected back and forth by the mirror-ends unit it stimulates an excited Ne atom and causes it to emit a fresh 6328-Å photon in phase with the stimulating photon. This process is cotinued and a beam of coherent radiation builds up in the tube. When this red-light bea becomes sufficiently intense, a portion of it escapes through the partially-silvered end.

(iii) Nd : YAG LASER (Nd : $Y_3Al_5O_{12}$). This is a solid state Laser in which $Y_3Al_5O_{12}$ (YAG) crystal is doped with Nd^{3+} ions [Neodymium]. In this Laser, electrons are excited to pump bands by absorption of photons from a flash lamp. Its main Laser transition occurs between ${}^4F_{3/2} \rightarrow {}^4I_{1/2}$ states. It lies in near infrared region with wavelength $1.06\,\mu m$. This is a 4-level laser. This is used for pumping in tunable lasers. It can give a power of 20-30 watt.

CAREER ENDEAVOUR



(iv) CO_2 LASER: It is a molecular laser. Energy-levels are quantised in vibrational and rotational levels. Active medium for CO_2 Laser is, $CO_2 : N_2 : He = 1 : 4 : 5$



CO_2 is not a tunable laser. It is 5 level laser. Lasing action taking place between vibrational states.

(v) He - Cd ≡ He - Ne Laser: In this Laser, active lasing-medium is Cadmium.

(vi) Semi-Conductor Laser: In this Laser, a p-n junction between direct band-gap semiconductor like GaAs is used. Wavelength of Laser Light $\lambda = \frac{hc}{E_g} = \frac{1242}{E_g\,(in eV)}$ nm, where E_g is the band gap energy.

It is solid state laser and tunable laser. If GaAs is doped with Aluminium or Phosphorous, its band-gap can be changed, hence λ of lasing light can be changed.

(vii) Dye-Laser: It can be constructed using an organic substance dissolved in water or methanol and this is a tunable laser.

Applications of Lasers:

(i) Laser in Science and Research

(ii) In Isotope Separation

(iii) Laser-Induced Fusion Reaction

(iv) Treatment of cancer, eyes, tumour, kidney stones.

CAREER ENDEAVOUR

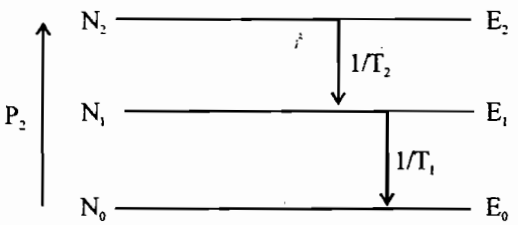
SOLVED PROBLEMS

1. In atomic system shown in the figure, the pump P_2 excites atoms from state 0 to state 2 at rate of 10^{20} atoms/cm^3–sec. Assume that

(1) State 0 is never depleted, $\frac{dN_D}{dt} = 0$

(2) Initial population densities N_1 and N_2 are two zero.

(3) Allowed decay rates with $T_2 = 1\,\mu s$, $T_2 = 2\,\mu s$ and neglect stimulated emission.

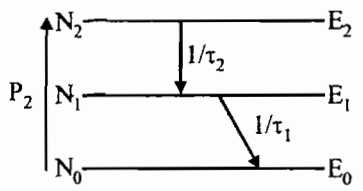


(a) Write the rate execution for states (2) and (1).

(b) Obtain the solutions for N_2CH and N_1CH.

(c) Steady state populations of state (2) and (1).

Soln. **(a)**



Pumping (Absorption) is always stimulated.

$$\frac{dN_2}{dt} = -B_{21}N_2 u(\nu) \quad \text{... (1)}$$

and $$\frac{dN_2}{dt} = -A_{21}N_2 \quad \text{... (2)}$$

$$= -\frac{N_2}{\tau_{21}} \quad \text{... (3)} \qquad \left[\because A_{21} = \frac{1}{\tau_{21}}\right]$$

By $$u(\nu) = \frac{\sigma I}{h\nu} \quad \text{... (4)}$$

where, σ is cross sectional area, I is intensity and ν is frequency.

From equations (1) and (4), we get $$\frac{dN_2}{dt} = -\frac{\sigma_{\text{emission}} I}{h\nu_2} N_2 - \frac{N_2}{\tau_{21}} + \frac{\sigma_{\text{absorption}} I N_o}{h\nu_0}$$

Coming to level positive, going far away from level negative,

$$\frac{dN_1}{dt} = +\frac{\sigma_{emission} I}{h\nu_2} N_2 + \frac{N_2}{\tau_{21}} - \frac{\sigma_{emission} I}{h\nu_1} N_1 \frac{N_0}{\tau_{10}}$$

$$\frac{dN_2}{dt} = P_2 - \frac{N_2}{\tau_2} \quad \text{... (1)}$$

$$\frac{dN_1}{dt} = \frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} \quad \text{... (2)}$$

(b) $N_2(t) = ?$, $N_1(t) = ?$, $N_1(0) = 0$, $N_2(0) = 0$

CAREER ENDEAVOUR

from equation (1), we have $\frac{dN_2(t)}{dt} = P_2 - \frac{N_2}{\tau_2}$ Let $P_2 - \frac{N_2}{\tau_2} = u$

$$\Rightarrow -dN_2 = \tau_2 du$$

$$-I_2 \frac{du}{u} = dt \Rightarrow \ln u = \frac{-t}{\tau_2} + C, \quad \text{At } t = 0,\ N_2(0) = 0$$

$\ln[P_2 - 0] = 0 + C \Rightarrow C = \ln P_2$

$$\ln\left[1 - \frac{N_2(t)}{P_2 \tau_2}\right] = -\frac{t}{\tau_2}, \quad 1 - \frac{N_2(t)}{P_2 \tau_2} = e^{-t/\tau_2}$$

$$\Rightarrow N_2(t) = (1 - e^{-t/\tau_2}) P_2 \tau_2$$

From equation (2), we have $\frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} = \nu$, $\ln \nu = -\frac{t}{\tau_1} + C$,

$$\Rightarrow \ln\left[\frac{N_2}{\tau_2} - \frac{N_1}{\tau_1}\right] = -\frac{t}{\tau_1} + C, \quad C = 0$$

$$\Rightarrow \frac{N_2}{\tau_2} - \frac{N_1}{\tau_1} = e^{-t/\tau_1}$$

$$\Rightarrow N_1 = \tau_1\left[\frac{N_2(t)}{\tau_2} - e^{-t/\tau_1}\right]$$

(c) In the steady state, the flow will be same, i.e.

$$\frac{dN_1}{dt} = 0 \quad .....(1),$$

and, $\frac{dN_2}{dt} = 0$ ..... (2)

$N_2 = P_2\tau_2$, $N_2\tau_1 = N_1\tau_2$

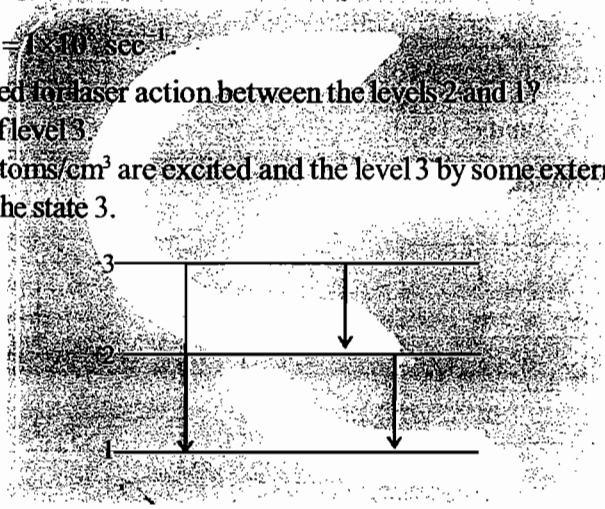
$N_2 = 10^{20} \times 10^{-6}$ atoms / m^3-sec = 10^{14} atoms / m^3 – sec

2. The figure shows the energy levels of 3 level atomic system with Einstein A coefficient $A_{32} = 7\times10^7\ sec^{-1}$, $A_{31} = 1\times10^7\ sec^{-1}$, $A_{21} = 1\times10^8\ sec^{-1}$.

(a) Can the system be used for laser action between the levels 2 and 1?

(b) What is the lifetime of level 3.

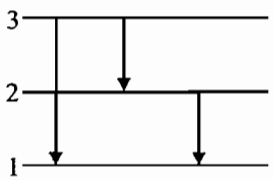
(c) At the time t = 0, N atoms/cm^3 are excited and the level 3 by some external mechanism, find the rate of change of population of the state 3.



CAREER ENDEAVOUR

Soln. **(a)** $A_{32} = 7 \times 10^7\ sec^{-1}$, $A_{31} = 1 \times 10^7\ sec^{-1}$, $A_{21} = 10^8\ sec^{-1}$, $\tau_2 = \frac{1}{10^8}$ sec

No Lasing action because this is a very low line state.



(b) Life-time of level 3,

$$\frac{1}{\tau_3} = \frac{1}{\tau_{32}} + \frac{1}{\tau_{31}} \qquad \text{... (1) (transition from level } 3 \rightarrow 2)$$

$$\because\ \tau_{32} = \frac{1}{A_{32}},\ \tau_{31} = \frac{1}{A_{31}} \qquad \text{... (2)}$$

$$\tau_3 = \frac{1}{A_{32} + A_{31}} = \frac{1}{8}\times10^{-7}\ \text{sec} = \boxed{1.25\times10^{-8}\ \text{sec}}$$

(c) Transitions $3 \rightarrow 1$ and $3 \rightarrow 2$ are spontaneous

$$\frac{dN_3}{dt} = -\frac{N_3}{\tau_{31}} - \frac{N_3}{\tau_{32}}$$

Condition $t = 0$, $N_3(0) = N$, $\frac{dN_3}{dt} = -N_3\left[\frac{1}{\tau_{31}} + \frac{1}{\tau_{32}}\right]$

$$\frac{dN_3}{N_3} = -\frac{1}{\tau_3}dt, \quad \ln N_3 = -\frac{t}{\tau_3} + C \Rightarrow C = \ln N$$

$$\boxed{N_3(t) = Ne^{-t/\tau_3}}$$

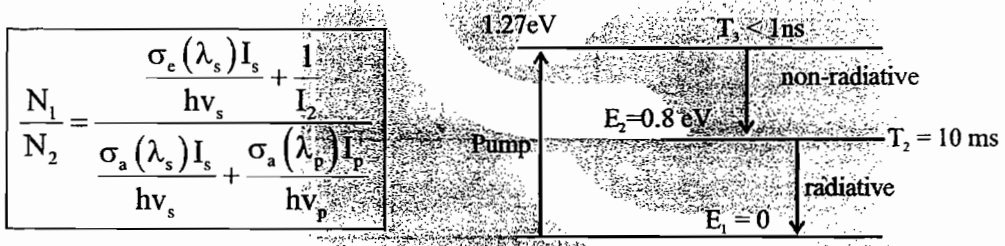
3. The level structure shown in the figure is for an Erbium-doped glass laser. The transition rates canbe expressed in terms of emission cross-section σ_e and the absorption coefficient σ_a as $\frac{dN}{dt} = \frac{\sigma I}{h\gamma}N$. Where I and γ are intensity and frequency of corresponding transition.

(i) What are the wavelengths λ_p and λ_s of the optical pump and signal respectively.

(ii) If N_1 and N_2 are population densities of states having energies E_1 and E_2 respectively, write rate equations in terms of $\sigma_e(\lambda_s)$, $\sigma_a(\lambda_s)$ and $\sigma_a(\lambda_p)$.

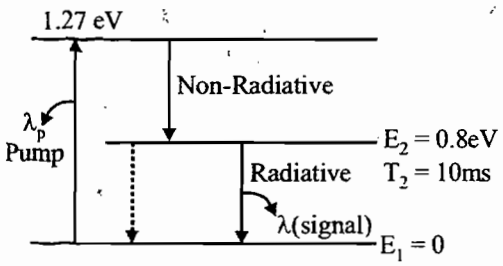
(iii) Show that under steady state conditions

$$\frac{N_1}{N_2} = \frac{\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{I_2}}{\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}}$$



Soln. **(i)** $\lambda_p = \frac{1240}{1.27eV}$ nm, $\lambda_s = \frac{1240}{0.8eV}$ nm

CAREER ENDEAVOUR



(ii) Reaching N_3 by stimulated absorption

$$\frac{dN_2}{dt} = \underbrace{\frac{\sigma_a(\lambda_p)I_pN_1}{h\nu_p}}_{\text{stimulated absorption}} - \underbrace{\frac{\sigma_e(\lambda_s)I_sN_2}{h\nu_s}}_{\text{stimulated emssion}} - \frac{N_2}{\tau_2} + \frac{\sigma_a(\lambda_s)I_sN_1}{h\nu_s} \quad \ldots (1)$$

$$\frac{dN_1}{dt} = -\frac{\sigma_a(\lambda_p)I_pN_1}{h\nu_p} + \frac{\sigma_e(\lambda_s)I_sN_2}{h\nu_s} + \frac{N_2}{T_2} - \frac{\sigma_a(\lambda_s)I_sN_1}{h\nu_s} \quad \ldots (2)$$

(iii) $\frac{dN_1}{dt} = 0 = \frac{dN_2}{dt}$ (steady state)

$$N_1\left[\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}\right] = N_2\left[\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{\tau_2}\right]$$

$$\boxed{\frac{N_1}{N_2} = \frac{\left[\frac{\sigma_e(\lambda_s)I_s}{h\nu_s} + \frac{1}{\tau_2}\right]}{\left[\frac{\sigma_a(\lambda_s)I_s}{h\nu_s} + \frac{\sigma_a(\lambda_p)I_p}{h\nu_p}\right]}}$$

4. Find $\frac{A}{B}$ ratio at room temperature for two levels with energy difference of 10.2 eV.

Soln. $\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}\frac{J\sec\sec^{-3}}{m^3\sec^{-3}}$ $\quad E = h\nu \Rightarrow \nu = \frac{10.2}{h}$

$$\frac{A}{B} = \frac{8\times3.14\times6.6\times10^{-34}\times(10.2)^3\times1.6^3\times10^{-57}}{(3\times10^8)^3\times(6.6\times10^{-34})^3}$$

$B \rightarrow \frac{m^3}{J-\sec^2}$, $A \rightarrow \sec^{-1}$

5. Calculate the relative rate of spontaneous and stimulated process in the microwave region ($\nu = 10^{10}$ Hz at 300K).

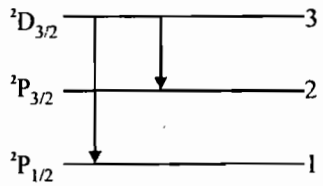
Soln. $\frac{NA}{NBu(\nu)} = \frac{\text{rate of spontaneous}}{\text{rate of stimulated}}$

$$\Rightarrow \frac{A}{Bu(\nu)} = (e^{h\nu/kT} - 1) = e^{\left(\frac{6.6\times10^{-34}\times10^{10}}{1.38\times10^{-23}\times300}\right)} - 1$$

CAREER ENDEAVOUR

6. In He-Cd Laser, transitions take place between $^2P_{3/2}$ and $^2D_{3/2}$ and $^2P_{1/2}$ with wave-lengths 353.6 and 325nm. $^2D_{3/2} \xrightarrow{353.6\text{nm}} {}^2P_{3/2}$ and $^2D_{3/2} \xrightarrow{325\text{ nm}} {}^2P_{½}$. The relative probability of radiative transmission are 1.6×10^5 $\sec^{-1}$ and 7.5×10^5 $\sec^{-1}$ respectively.

Soln. $A_{31} = 7.5 \times 10^5$ $\sec^{-1}$, $A_{32} = 1.6 \times 10^5$ $\sec^{-1}$



Life Time of $^2D_{3/2} = \tau_3$ = level-3 life time

$$\frac{1}{\tau_3} = (7.5 \times 10^5 + 1.6 \times 10^5) = 9.1 \times 10^5 \sec^{-1}, \quad \tau_3 = \frac{1}{9.1\times10^5} \text{ sec}$$

7. In a He-Ne laser, the laser transition takes place in **[GATE 2007]**
   (a) He only (b) Ne only
   (c) Ne first, then in He. (d) He first, then in Ne

Soln. In a He-Ne laser (Four level laser), the population inversion is achieved by electric discharge He atoms help in achieving a population inversion in the Ne atoms.
Thus, the laser transition takes place in Ne only.
Hence, correct option is (b).

8. The coherence length of laser light is : **[GATE 2008]**
   (a) Directly proportional to the length of the active medium
   (b) Directly proportional to the width of the spectral line
   (c) Inversely proportional to the width of the spectral line
   (d) Inversely proportional to the length of the active lasing medium

Soln. The coherence length (L) of laser light is the that light travels in coherence time (τ) is $L = \tau C$ where C is speed of light and τ is coherence time.
Thus, coherence length is directly proportional to the length of the active lasing medium.
Hence, correct option is (a).

9. The population inversion in a two level laser material cannot be achieved by optical pumping because
   (a) the rate of upward transitions is equal to the rate of downward transitions. **[GATE-2011]**
   (b) the upward transitions are forbidden but downward transitions are allowed.
   (c) the upward transitions are allowed but downward transitions are forbidden.
   (d) the spontaneous decay rate of the higher level is very low.

Soln. In case of two level, the rate of upward transitions is equal to the rate of downward transitions which gives $N_2 = N_1$.
Thus, there will be no population inversion.
Hence, correct option is (a).

10. A three level system of atoms has N_1 atoms in level E_1, N_2 in level E_2 and N_3 in level E_3 ($N_2 > N_1 > N_3$) and $E_1 < E_2 < E_3$. Laser emission in possible between the levels **[GATE - 2005]**
    (a) $E_3 \rightarrow E_1$ (b) $E_2 \rightarrow E_1$ (c) $E_3 \rightarrow E_2$ (d) $E_2 \rightarrow E_3$

Soln. Here, in the given three level system of atoms, the level with energy E_2 has largest atoms N_2 amongest all three levels, which confirms that this is a metastable state. Similarly, E_1 and E_2 represents the ground and excited state repectively. Thus, the laser emission will be possible only between E_2 to E_1 levels.
Hence, correct option is (b).

CAREER ENDEAVOUR

11. Which one of the following electronic transitions in neon is not responsible for LASER action in Helium-Neon laser ? **[GATE - 2006]**

(a) $6s \rightarrow 5p$ (b) $5s \rightarrow 4p$ (c) $5s \rightarrow 3p$ (d) $4s \rightarrow 3p$

Soln. For He-Ne laser the laser transition takes place in Ne only.

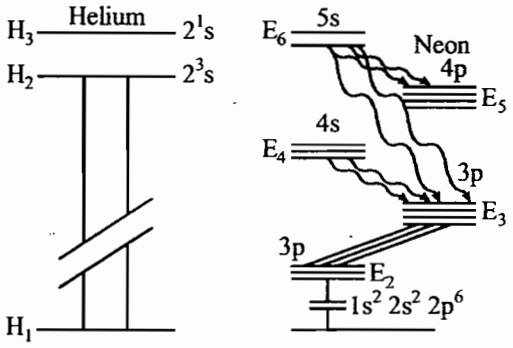


Figure : (Relevant energy level of the He-Ne laser)

According to above diagram, the electronic transition $6s \rightarrow 5p$ is not responsible for LASER action in He-Ne laser.

Hence, correct option is (a).

12. When the refractive index m of the active medium changes by $\Delta\mu$ in a laser resonator of length L, the change in the spectral spacing between the longitudinal modes of the laser is (c is the speed of light in free space)

(a) $\dfrac{c}{2(\mu+\Delta\mu)L}$ (b) $\dfrac{c}{2\Delta\mu L}$ (c) $\dfrac{c}{2L}\dfrac{\Delta\mu}{\mu(\mu+\Delta\mu)}$ (d) zero **[GATE 2008]**

Soln. Relation between refractive index and velocity is given by

$$\mu = \frac{c}{v} \qquad \text{... (i)}$$

where, c is speed of light in vacuum and v is speed of light in medium of refractive index μ.

$$\Rightarrow \quad v = \frac{c}{\mu}$$

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For laser resonator of length L, the time (t) of the laser resonator to cover length (L) is given by

$$t = \frac{L}{v} = \frac{L\mu}{c} \text{ and frequency is } v = \frac{1}{t} = \frac{c}{L\mu}$$

when the refractive index changes from μ to μ' and velocity v changes from v', then

$$v' = \frac{c}{\mu'} = \frac{c}{(\mu+\Delta\mu)} \quad (\text{Let } \mu' - \mu = \Delta\mu)$$

$$\text{Thus, } t' = \frac{L}{v'} = \frac{L(\mu+\Delta\mu)}{c} \text{ and the frequency is } v' = \frac{c}{L(\mu+\Delta\mu)}$$

Now, change in velocity;

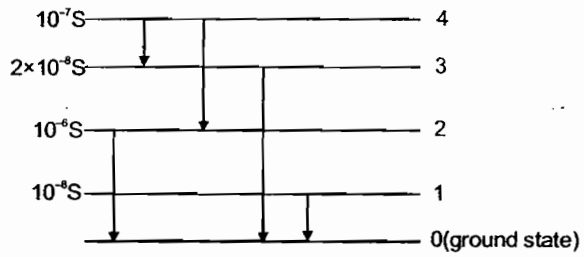
$$\Delta v = v - v' = \frac{c}{L}\left(\frac{1}{\mu} - \frac{1}{(\mu+\Delta\mu)}\right) = \frac{c}{L}\frac{\Delta\mu}{\mu(\mu+\Delta\mu)}$$

Therefore, spectral spacing between longitudinal modes is

$$= \frac{\Delta v}{2} = \frac{c\Delta\mu}{2L\mu(\mu + \Delta\mu)}$$

Hence, correct option is (c).

13. Five energy levels of a system including the ground state are shown below. Their lifetimes and the allowed electric dipole transitions are also marked.



Which one of the following transitions is the most suitable for a continuous wave (CW) laser?

(a) $1 \rightarrow 0$ (b) $2 \rightarrow 0$ (c) $4 \rightarrow 2$ (d) $4 \rightarrow 3$ **[GATE-2009]**

Soln. In all the transitions given above, the transition from $2 \rightarrow 0$ is the most suitable for a continuous wave (cw) laser because the state 2 is a metastable state with highest life time of 10^{-6} sec.

Hence, correct option is (b).

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